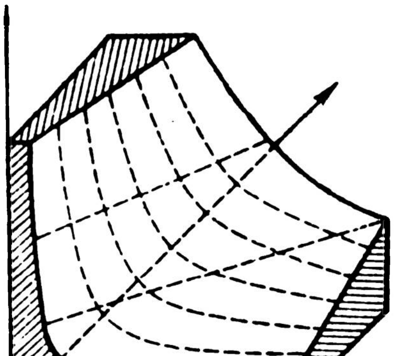
Fundamentals of Chemical Thermodynamics

E.N. Yeremin



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E.N. Yeremin

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На английском языке

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Preface

> All the causes of a phenomenon in all their entirety are inaccessible to the human mind. But the urge to discover these causes is deeply rooted in the man's soul.
>
> *L. Tolstoy*

This book is based on lectures in physical chemistry given by the author for many years to students of chemistry at Moscow State University. As its title implies, the book is a text on thermodynamics designed primarily for chemists and is intended as a part of a general course in physical chemistry. In distinction to the traditional presentation of chemical thermodynamics, in this book a great deal of attention is paid to the interrelationships between thermodynamics and other sections of physical chemistry, in the first place physical statistics, more exactly statistical methods in thermodynamics. These methods have been extensively developed recently and are most suitable for calculations of chemical equilibria in gases at high temperatures. The applicational aspects of statistical thermodynamics require a knowledge of the energy levels of molecules. This knowledge comes, first, from experiment, primarily spectroscopy, electron diffraction studies, nuclear magnetic resonance, and the methods involving the electrical properties of molecules. Second, substantial data are provided by quantum mechanics employed at the various levels of approximation. Therefore, in this book ample space is devoted to these areas, the material presented being reduced to a minimum required for building up the relationship to thermodynamics.

The treatment of classical thermodynamics, on which the book rests, is naturally based on the first, second, and third laws. To these is added the fourth law, which is known as the zeroth law of thermodynamics. Apart from the classical statements of the second law of thermodynamics, the author has also used the Carathéodory formulation, which is thought by the author to be logically the most rigorous.

Special emphasis is made throughout the book on the entropy as the most important thermodynamic function that determines the condition for equilibrium and spontaneity of the change of an (isolated) system. But the study of equilibria itself is carried out at constant pressure and temperature with the aid of a subsidiary function—the Gibbs free energy.

The book offers a description of a number of present-day methods of calculation of chemical equilibria, including the equilibrium of the dissociation of (diatomic) molecules into atoms and the equilibrium of ionization at high temperatures upon transition of substances to the plasma state.

One of the author's aims in preparing this text has been to expound thermodynamics in the simplest form possible, without cutting down consideration of physical concepts.

The first edition of this book was published in 1974. The second edition gives a more up-to-date exposition of the basic laws of thermodynamics. For example, the first law is applied at the very beginning to multicomponent systems, for which purpose a chemical variable (the extent of reaction) is introduced. Some methodological changes have been made in the treatment of the second law and its applications. Phase transitions of the second kind are dealt with in more detail. The last chapter on the application of thermodynamics to non-equilibrium (irreversible) processes has been enlarged to a certain extent and new material pertaining to calculations has been added.

The author has a great pleasure to express his gratitude to Ya. I. Gerasimov, a Corresponding Member of the USSR Academy of Sciences for reading the manuscript and making valuable suggestions. My special thanks go to E. A. Rubtsova (Candidate of Chemical Sciences) who contributed so generously of her time in reading the entire manuscript and in making a host of corrections and suggestions to improve the clarity of the presentation.

The author is greatful to Professor L. A. Nikolaev for helpful comments and to his colleagues at the Chemistry Department of Moscow University—V. M. Belova and V. K. Matveev—for their help in the preparation of the second edition. The author is also indebted to M. M. Poplavskaya, the editor of the second edition (in Russian), for her work on improvement of the text.

Finally, the author wishes to express his appreciation to the readers who called and will call attention to the inevitable errors, which, despite all effort and care, still manage to escape detection.

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Chapter I

General Concepts and Equations of State

1.1. Introduction

Chemical thermodynamics is one of the branches of physical chemistry and that is why we shall first define this science as a whole. Physical chemistry is a science concerned with establishing relationships between physical and chemical phenomena and between the physical and chemical properties of substances. But the establishment of such relationships is not an objective in itself. Using these relationships, physical chemistry works out general regularities governing chemical transformations and making it possible to predict the possible direction of a reaction and the final result of a chemical interaction.

What physical phenomena are meant in this case? We mean thermal, electrical, light and other phenomena. Thus, we know well that chemical reactions are accompanied by the evolution or absorption of heat. For example, the synthesis of ammonia from simple substances belongs to exothermic reactions:

$$N_2+3H_2 \rightarrow 2NH_3 \quad Q=-22.08 \text{ kcal/2 moles } NH_3 \tag{1.1}$$

On the contrary, the formation of nitrogen oxide from nitrogen and oxygen proceeds with the absorption of heat, i.e., the reaction is endothermic:

$$N_2+O_2 \rightarrow 2NO \quad Q=+43.2 \text{ kcal/2 moles NO} \tag{1.2}$$

The objective of physical chemistry, more exactly thermochemistry and thermodynamics, is to determine the *heat effects* of chemical reactions, their dependence on the reaction conditions, primarily on temperature. A study of thermal phenomena that accompany chemical reactions and also of some *thermal* properties of reacting substances, namely their *entropy* and *heat capacity*, allows one to establish the general criteria of spontaneity of reactions and also criteria of equilibrium. Here, on the basis of certain approximations it is possible to derive one of the most important laws of chemistry—the law of mass action, which was enunciated by Guldberg and

Waage (1867) on the basis of other, different assumptions.* The essence of the matter can be reduced to the possibility of a theoretical calculation of the equilibrium constant (K_p) and the determination of the equilibrium state of the reacting system and, hence, the highest (possible under given conditions) yield (concentration) of the product of interest.

Returning to the synthesis of ammonia (1.1), it should be recalled that it is reversible and that the equilibrium concentrations of the reactants depend on the reaction conditions, i.e., in the first place on the temperature (T) and the total pressure (P). Table 1.1 gives the equilibrium concentrations of ammonia (in mole per cent) for two temperatures and three pressures, which were obtained by F. Haber at the turn of the century. From Table 1.1 it follows that the synthesis of ammonia must be carried out at as high a pressure and as low a temperature as possible. The second recommendation suggested by thermodynamics cannot be fully realized. Another branch of physical chemistry, chemical kinetics, suggests that the rate of a chemical reaction falls off very rapidly with decreasing temperature. On the other hand, according to kinetic data the reaction rate can be increased by using catalysts. According to the results of a detailed physico-chemical study, the synthesis of ammonia is carried out at a temperature of 450-500°C using catalysts consisting of metallic iron and some activators (promoters).

TABLE 1.1. **Equilibrium Concentrations of Ammonia under Various Conditions**

t, °C	Mole per cent of NH_3 at pressures (in atm)			Increase in NH_3 concentration with increase in pressure from 1 to 600 atm
	1	100	600	
400	0.51	27.3	57.1	110
500	0.06	5.2	21.6	360

The most important interrelated concepts in thermodynamics are *energy*, *heat* and *work*. These concepts are examined in detail in Chapter 3. Here we shall only point out that the term "thermodynamics" derives from the Greek words *therme* (heat) and *dinamis* (force). Therefore, the word thermodynamics should be translated as a "science of the forces associated with heat" (and not as a science of the transfer of heat). However, at the time of the origin of thermodynamics (19th century) the scientists did not always clearly differentiate between "force" and "energy". As to the definition of the term, thermodynamics is a field concerned with the study of the interconversion of heat, work and various kinds of energy, which are collectively termed the *internal energy*. The general laws deduced in thermodynamics are used in various branches of science. Applications of these laws to chemistry are in the realm of *chemical thermodynamics*—the subject matter of the present book.

---

* The discovery of the law of mass action was closely approached by N. N. Beketov in his works on the displacement of metals by hydrogen from aqueous solutions of salts (1860).

Classical (phenomenological) thermodynamics is based on a very limited number of postulates deduced from experiments and observations. In particular, the enunciation of the first law of thermodynamics is associated with the unsuccessful attempts to construct a machine capable of producing energy, a so-called "perpetual-motion machine", which unfortunately continue up to the present time. From these postulates, by a purely logical and mathematical means, there are established numerous special regularities that allow us to predict the possible direction of various kinds of processes and the properties of substances. There is no place here for hypotheses and models.

At a later time, statistical thermodynamics was developed, which is based on molecular-kinetic concepts and, in the first place, on an ideal-gas model. Methods of statistical thermodynamics make extensive use of data on the molecular structure of a substance found both experimentally with the aid of spectroscopy, electron diffraction studies, X-ray diffraction analysis and other physical methods, and theoretically by means of quantum mechanics.

This book begins with a consideration of the general regularities of thermodynamics and their application to chemistry, more exactly to the study of chemical equilibria along classical lines. This is followed by a description of statistical methods of determining the thermodynamic functions based on the results obtained by quantum mechanics. Chapters 7 and 8 are devoted to solutions and the phase rule, the treatment being also based on classical conceptions, and the last chapter deals with the application of thermodynamics to nonequilibrium (irreversible) processes.

1.2. A System. The State of a System. Equations of State. Partial Molar Quantities. A Chemical Variable

The concrete material object of a thermodynamic investigation is a *thermodynamic system* or simply a *system* by which we mean a certain portion of the physical universe, large or small, enclosed by real or imaginary boundaries and thus separated from the rest of the universe, which we shall call the surroundings. A system may take the form of a gas in a cylinder, a solution of reagents in a flask, a crystal of a substance or even a mentally isolated small portion of objects.

A system is called *homogeneous* if it has the same chemical composition and physical structure at all its points; in fact, one can speak of a *phase*.

For example, a mixture of gases or vapours and a solution are homogeneous single-phase systems. A system is called *heterogeneous* if it consists of two or more phases. A phase is defined as a part of a system, uniform throughout in chemical composition and physical properties, which is separated from other homogeneous parts of the system by boundary surfaces. For example, in some cases water (or any other substance) is capable of forming a system consisting of three phases. If in the system ice, liquid water, including all drops on the walls or lid of the vessel, and water vapour coexist, then each form constitutes a separate phase, and each phase is separated from every other by a phase boundary. The system is thus a heterogeneous, three-phase system. Let us consider the reduction of ferrous oxide by hydrogen in a closed vessel:

$$\text{FeO (solid)} + H_2 \rightarrow \text{Fe (solid)} + H_2O \text{ (vapour)}$$

Here the solid ferrous oxide forms one phase and the solid iron is another phase since they are mutually immiscible and, hence, crystallize separately. On the other hand, a homogeneous mixture of hydrogen and water vapour forms a third phase.

There are also *continuous systems*. No interfaces are present in them, but some of the characteristics continuously change from point to point. For example, in a metal bar, whose ends are subjected to different temperatures, a certain temperature gradient sets in. In a vertical gas column the pressure will change continuously with height from point to point approximately according to the Laplace formula:

$$P = P_0 e^{-mgh/kT}$$

Regions outside the boundaries of a system constitute the *surroundings*. A system which does not interact with its surroundings, i.e., cannot exchange either matter or energy with the surroundings, is called an *isolated system*.

A *closed system* is one in which no transfer of matter to or from the surroundings is possible, but that of energy is. In this book we shall deal with closed systems and partly with isolated systems. A system which can exchange both matter and energy with its surroundings is said to be *open*.

Chemical substances that enter into the composition of a system are termed *components* (a stricter concept of the term "component" will be given in Chapter 8). A system consisting of a single substance, say water, is called a one-component system; a system composed of two components is known as a two-component or binary system. Let a system be composed of 1, 2, . . . *c* components and their masses be

$m_1, m_2, \ldots, m_c$. The total mass of the system

$$m = \sum_{i=1}^{c} m_i$$

In order to characterize the chemical composition of a system, the following concentration units are used:

1. The *mass fraction* of component i is $\chi = m_i/m$; 100χ will constitute a mass per cent.

2. If the number of moles of component i is $n_i = m_i/M_i$, where M_i is the molar mass, then $x_i = n_i/\sum n_i$ will express its mole fraction and $100\, x_i$ will be a mole per cent. It is clear that

$$\sum_{i=1}^{c} \chi_i = \sum_{i=1}^{c} x_i = 1$$

3. If the volume of a homogeneous system (phase) is v, then $C_i = n_i/v$ will express the *molarity* of component i or its *molar concentration*. The last concentration unit is especially important in chemical kinetics.

A system is characterized by a number of inherent *thermodynamic properties*: mass m, volume v, pressure p, temperature T, density ρ, concentration C, etc.* The properties of the system fall into two essentially different, distinct classes: intensive and extensive. *Extensive properties* or *variables* have magnitudes proportional to the total amount of material under consideration. Examples of such properties are total mass, volume, and energy; the total volume, mass, etc., of two systems are equal to the sum of the volumes, masses, etc., of these systems taken separately. *Intensive properties* or *variables* have magnitudes simultaneously characteristic both of the whole system and of any arbitrarily chosen macroscopic portion of it. An intensive variable measures an inherent property of a system, a property whose value does not depend on the size of the system. Intensive variables are exemplified by quantities such as temperature, pressure, and concentration. There is a bridge between the two classes of properties, since an extensive property referred to unit volume or mass changes into an intensive property (molar volume, density, chemical potential, etc).

All these properties taken together determine the *state of a system*. Thus, a knowledge of the state of a system presupposes a knowledge of its properties. However, in order to characterize the state of a system unambiguously there is no need to specify all its properties or the greater part of them. The point is that the properties of a system are not independent. There exist certain functional relations between them. Therefore, *in most cases it will suffice to specify only a few of the properties of a system and the remaining properties will appear to be strictly defined.* If we deal with homogeneous systems consisting of a pure substance of known mass, it will suffice to specify any two of its properties in order to define completely the state of the system. Any two of the three variables—the molar* volume $\underline{v}$, pressure p and temperature T—are chosen for the purpose.

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* One also speaks of the "state parameters" or "state variables", meaning what are called "properties" in this book.

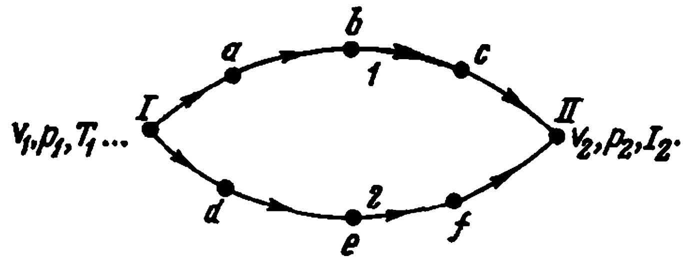

Fig. 1.1. The change of the state of a system. (The state of the system characterized by the properties $\underline{v}$, p, and T is designated by a dot.)

These variables are connected by an equation called the *equation of state*; in a general form it is written as follows:

$$f(p, \underline{v}, T) = 0 \tag{1.3}$$

The simplest equation of state is the equation of state for an ideal gas:

$$p\underline{v} = RT \tag{1.4}$$

If n moles of gas is considered, then we have

$$pV = nRT \tag{1.5}$$

where V is the volume of n moles; R is the universal gas constant in both cases; it will be considered in more detail at a later time.

Imagine a system which is in state I (Fig. 1.1) characterized by the values of the variables v_1, p_1, T_1, ... When subjected to external influences—compression, expansion, heating, etc.—the system undergoes changes, passing through intermediate states, including the states a, b, c, ..., and assumes the final state II defined by the values of the variables v_2, p_2, T_2, etc.

The set of intermediate states (generally speaking, their number may be infinite) is called *the path by which the system is changed.* The states a, b, c, ... lie on the first path. However, by changing the character and sequence of the action on the system it is possible to convert it from the first state to the second by a different path, say the path (2), which includes the intermediate states d, e, f, etc.

---

* Throughout the book extensive quantities per mole will be designated by a bar placed under the symbol.

An essential point here is that the overall change in one of the properties of the system, say its molar volume

$$\underline{v}_2-\underline{v}_1=\Delta\underline{v} \qquad (1.6)$$

or pressure $p_2 - p_1 = \Delta p$, does not depend on the path by which the system passes from the first state to the second but is determined only by these states. We are speaking here of these seemingly self-evident things only because, first, not all the properties of a system are so spectacular as the volume and pressure. And, second, the reader will soon have to deal with quantities which are also very important and which are not the properties of a system. The numerical values of these quantities will be determined by the nature of the path by which the system is transformed.

From a mathematical point of view the statement that the change of a property is independent of the path involved is tantamount to the following proposition: an infinitesimal change in a property of a system is an *exact differential.* Indeed, any property of a system can be represented, at least in a general form, as a function of some other properties. For example,

$$\underline{v}=f(p, T) \qquad (1.7)$$

This function can be differentiated:

$$d\underline{v}=df(p, T)=\left(\frac{\partial v}{\partial p}\right)_T dp+\left(\frac{\partial v}{\partial T}\right)_p dT \qquad (1.8)$$

Thus, an infinitesimal change in the property will in fact be expressed by an exact differential.

With a finite change of the system, say, when the system goes from state I to state II (see Fig. 1.1), the total change of the property will be summed up of slight changes on infinitesimal portions of the path. In other words, the overall change in the property can be represented by an integral:

$$\int_1^2 d\underline{v}=\int_1^2 df(p, T)=\underline{v}_2-\underline{v}_1=\Delta\underline{v} \qquad (1.9)$$

According to the theorem of mathematical analysis, the integral of the exact differential is independent of the path of integration. Hence, the statement that the change of a property is independent of the path used in the process may be replaced by an equivalent one: the change in a property is an exact differential. The converse is also true: if the change in some quantity is independent of the conversion path, then this quantity is a property of the system.

Let us now return to simple equations of state and the gas constant. The product of pressure and volume has the dimensions of work:

$$p\left[\frac{\text{force}}{\text{length}^2}\right] v\,[\text{length}^3] = [\text{force}\cdot\text{length}] = \text{work}$$

Hence, solving Eq. (1.4) for R, we have

$$R = \frac{pv}{T} = \left[\frac{\text{work}}{\text{mole}\cdot\text{deg}}\right] \tag{1.10}$$

Under normal or standard conditions, i.e., 0°C or 273.15°K and 1 atm, one mole of an ideal gas occupies a volume of 22.414 litres. Thus,

$$R = \frac{1\times 22.414}{273.15} = 0.08206\,\frac{\text{litre}\cdot\text{atm}}{\text{mole}\cdot\text{deg}} \tag{1.11}$$

Here use is made of the unit of work (litre·atmosphere) used in thermodynamics. It is easy to convert an atmosphere to dynes/cm^2: 1 atm = 76 cm Hg × 13.595 = 1033.2 g/cm^2 × 981 = 1.013 × × 10^6 dynes/cm^2. Now we obtain

$$R = \frac{1.03\times 10^6\times 22.414}{273.15} = 8.314\times 10^7\,\frac{\text{ergs}}{\text{mole}\cdot\text{deg}} = 8.314\,\frac{\text{joules}}{\text{mole}\cdot\text{deg}} \tag{1.12}$$

At present the basic unit of the quantity of heat is the joule.* However, the calorie is also used, but it is not referred to the heating of water and is defined simply by the relation

$$1\ \text{calorie} \equiv 4.1840\ \text{absolute joules} \tag{1.13}$$

and therefore

$$R = 1.987\ \text{cal}\cdot\text{mole}^{-1}\cdot\text{deg}^{-1} \tag{1.14}$$

The equation of state of an ideal gas (1.4) can also be approximately applied to real gases only if the pressure is not too high and the temperature not too low. Gases such as nitrogen and oxygen under ordinary conditions obey Eq. (1.4) with an accuracy of up to a few tenths of a per cent. Numerous problems in physical chemistry are solved with the aid of this equation, though with a lesser accuracy. For example, Eq. (1.5) can be written as follows:

$$pV = nRT = \frac{g}{M}RT \tag{1.15}$$

---

* According to the International System of Units (SI), the unit of energy, work and heat is the *joule*. However, since most of the handbooks on thermochemical and thermodynamic quantities still make use of the *thermochemical calorie*, we think it expedient to retain in this textbook the same system of units in order to avoid confusion that might arise.

Apart from the thermochemical calorie defined by Eq. (1.13), which is exclusively employed in this book, use is also made of the "technical calorie" equal to 4.1868 J.

where g is the weighed amount of substance and M is its molar mass. Having produced, at a known temperature, a substance in the gaseous (vapour) state and measured the volume and pressure, we can determine its molar mass (the method due to V. Mayer). It would not be an exaggeration if we assert that classical physical chemistry and thermodynamics are wholly based on the ideal gas law in all their applications.

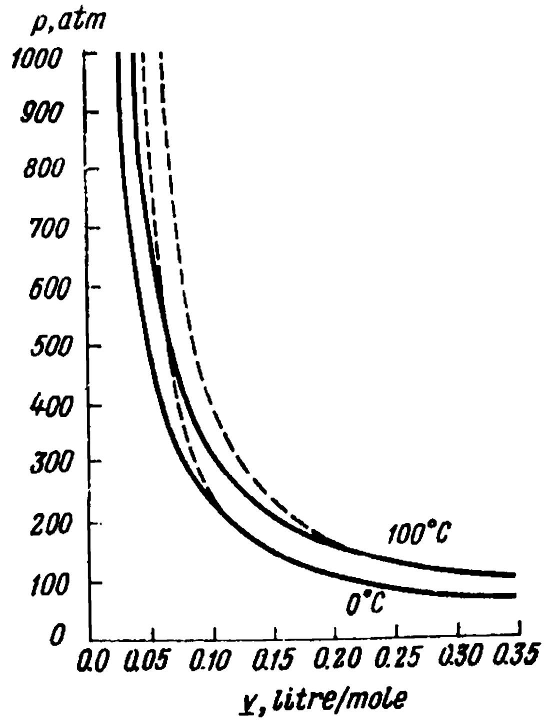

Fig. 1.2. The isotherms of an ideal and a real gas:

Solid curves represent hyperbolas constructed according to the equation $pv = RT$; dashed lines—real isotherms for nitrogen.

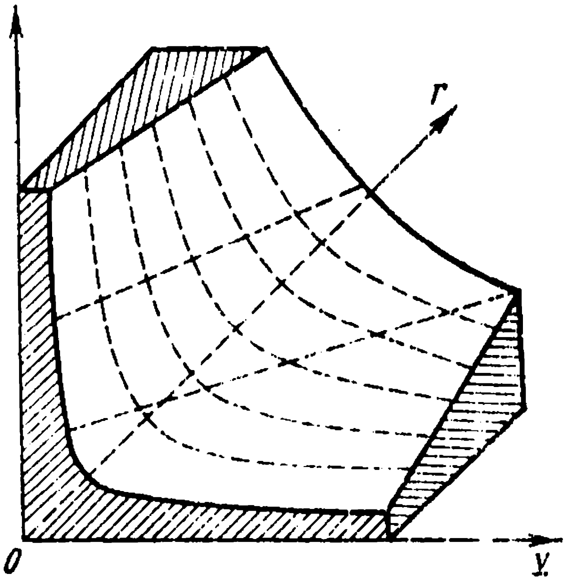

Fig. 1.3. The p-v-T surface for an ideal gas, which is a graphical representation of the equation of state $pv = RT$.

In thermodynamics and physical chemistry the functional relationships are often pictured by graphical methods. In particular, wide use is made of *isotherms*. An example is the dependence of the volume of a gas on pressure at constant temperature:

$$v = f(p) \qquad (T = \text{const}) \tag{1.16}$$

For an ideal gas the relation

$$v = \frac{RT}{p} = \frac{\text{const}}{p}$$

is an equilateral hyperbola, whose position depends on temperature. Figure 1.2 shows two isotherms for an ideal gas at 0°C and 100°C. The same figure gives the experimental (actual) isotherms for nitrogen. The broken curves pertaining to nitrogen depart noticeably from ideal isotherms in the region of high pressures where the compressibility of a real gas is lower than that of an ideal gas and the pressure increases more rapidly with decreasing volume. As the pressure falls the solid and broken curves merge (on the given scale), i.e., as the pressure decreases (the temperature increases) the properties of a real gas approach those of an ideal gas.

If we consider the equation $pv = RT$ as a whole as the p-v-T relation, it will be depicted graphically by a surface (Fig. 1.3). Some intersections of the surface with the planes corresponding to constant temperatures are shown in this figure by broken lines.

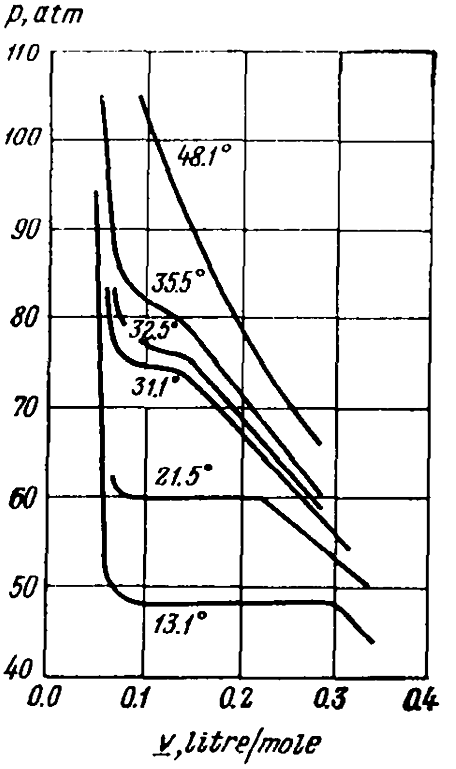

Fig. 1.4. Isotherms for carbon dioxide: the critical isotherm corresponds to 31.1°C = t_{cr}.

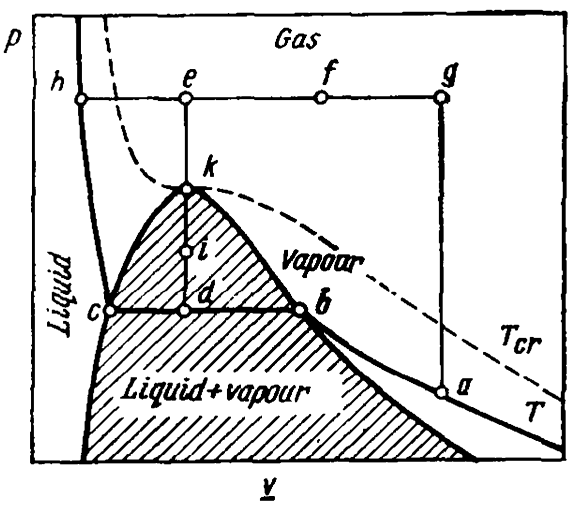

Fig. 1.5. Schematic phase diagram for the system vapour-liquid.

The departure of the behaviour of a real gas from that of an ideal gas increases also with decreasing temperature. Figure 1.4 shows a number of isotherms for carbon dioxide. As can be seen from Fig. 1.4, at temperatures below 31.3°C horizontal portions appear on the isotherms corresponding to regions where vapour and liquid coexist (a two-phase system). The phenomena observed here are better traced from Fig. 1.5. The broken curve in this figure shows a *critical isotherm*, i.e., an isotherm at a critical temperature above which a gas cannot be converted into a liquid by any compression. If one mole of gas present at point *a* is compressed at constant temperature (in Fig. 1.4 the corresponding isotherm for carbon dioxide is marked by a temperature of about 21°C), then the decrease in volume is first accompanied by an increase in pressure, but starting from the state corresponding to point *b* the further decrease in volume occurs at constant pressure. Generally speaking, at this temperature the substance is not a gas but a vapour, which becomes saturated at point *b*. Along the straight line *b-c* the vapour is subjected to condensation. The volume corresponding to point *b* is the molar volume of the saturated vapour, $\bar{v}_{\text{vap}}$, and at point *c* it is the molar volume of the liquid, $\bar{v}_{\text{liq}}$.

A sharp increase in pressure from point *c* is associated with the low compressibility of the liquid. At higher temperatures an analogous curve appears but its horizontal portion, i.e., the region where liquid and vapour coexist in equilibrium, becomes shorter and disappears at all at the critical temperature. In Fig. 1.5 the region of two-phase systems (liquid and vapour) is shaded. The point lying at the top of the region where vapour and liquid coexist in equilibrium is called the *critical point*. In *p-v* diagram it is represented in the coordinates—the critical volume $\bar{v}_{\text{cr}}$ and the critical pressure p_{cr}, which, along with the critical temperature, are quantities that characterize a substance. The values of the critical quantities for some substances are given in Table 1.2.

TABLE 1.2. **Critical Quantities for Selected Substances**

Substance	T_{cr}, °K	p_{cr}, atm	v_{cr}, cm³/mole	Substance	T_{cr}, °K	p_{cr}, atm	v_{cr}, cm³/mole
Ar	150.87	48.34	74.56	SO_2	430.25	77.65	430.7
Cl_2	417.1	76.1	123.4	SO_3	491.4	83.8	126.5
CO	134.4	34.6	90.03	Xe	289.9	58.2	118.8
CO_2	304.18	72.83	94.23	CCl_4	556.25	44.82	275.8
CS_2	546.15	72.87	172.7	CCl_2F_2	385	39.6	218
HCl	324.6	81.6	86.0	CH_4	190.25	45.6	98.77
He	5.23	2.26	61.55	CH_3Cl	416.2	65.92	136.4
Hg	1735	1042	40.12	CH_3OH	513.1	78.50	117.7
H_2	33.2	12.8	69.68	C_2H_2	308.6	61.65	112.9
H_2O	647.3	218.5	55.44	C_2H_4	282.8	50.55	126.1
D_2O	644.6	218.6	55.16	C_2H_6	305.7	48.7	141.7
Kr	209.39	45.18	92.08	CH_3COOH	594.7	57.11	171.2
Ne	44.75	26.86	44.30	C_2H_5OH	516.2	62.95	167.2
NH_3	405.5	112.2	72.02	CH_3COCH_3	508.5	46.6	213
N_2	125.97	33.49	90.03	n-C_5H_{12}	470.3	33.04	310.2
NO	177.1	64	57.25	C_6H_6	516.6	47.89	256.4
N_2O	311.9	77.5	96.92	n-C_6H_{14}	507.9	29.62	367.4
O_2	154.28	49.71	74.42	C_6H_5Cl	632.3	44.64	307.8
Rn	377.5	—	—	n-C_7H_{16}	539.95	26.88	427.7
$SnCl_4$	591.8	33.95	351.2	$C_6H_5CH_3$	593.8	41.6	315

Thus, let the path *abdch* of the conversion of vapour to liquid pass through a heterogeneous region where the system is separated into two phases—the liquid and the vapour phase. But, following the path *agfeh* the vapour can also be converted to the liquid by-passing the heterogeneous regions, i.e., without the system being separated into two phases.

Suppose now that we have a sealed test tube containing a liquid and a vapour in a state corresponding to point *d*. The liquid and the vapour are separated by a meniscus. If the system is led from point *d* along the path *dike*, i.e., if the temperature is raised, the meniscus will disappear at point *k*—at the critical point the properties of the vapour and the liquid are identical. It is essential that we visualize the changes in the densities of the liquid and vapour along the path *dik*. As the temperature increases the density of the liquid decreases as a result of an ordinary thermal expansion; as regards the saturated vapour, its density, on the contrary, increases due to the vaporization of part of the liquid and to the increase in the total pressure of the system. In this connection, it will be useful to consider the empirical law of the rectilinear diameter (the Cailletet and Mathias law), according to which the mean density of a liquid and a saturated vapour is a linear function of the temperature, i.e.,

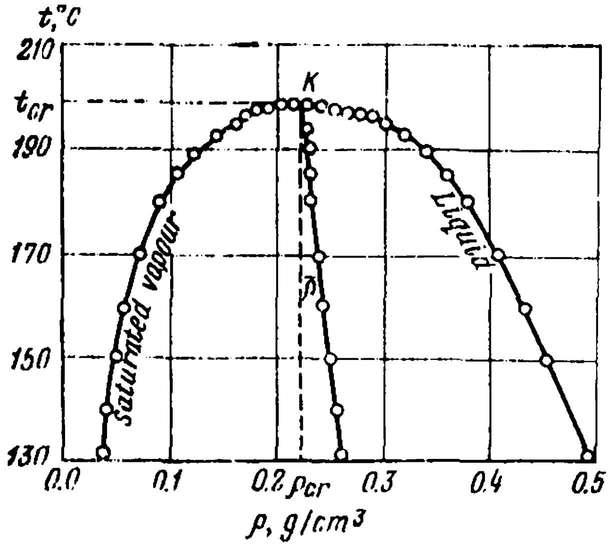

Fig. 1.6. Dependence of the densities ρ of a liquid and a vapour on temperature T for normal pentane.

$$\bar{\rho} = \frac{1}{2}(\rho_{\text{liq}} + \rho_{\text{vap}}) = A + Bt \tag{1.17}$$

where A and B are constants for a given substance. This rule is illustrated in Fig. 1.6 which shows the temperature dependences of the densities indicated above for normal pentane. As can be seen from Fig. 1.6, the density curves merge at the critical point. It can be pointed out that measurements of densities (for specific volumes) at temperatures close to the critical temperature are difficult to carry out and that the critical temperature can be determined with a rather high accuracy by observing, for example, the disappearance of the meniscus. Therefore, the law of the rectilinear diameter is conveniently used for the determination of the critical density (the critical volume) by extrapolating the $\bar{\rho}$ straight line to the critical temperature.

As we already know, Eq. (1.5) does not reflect the behaviour of real gases, especially at temperatures below the critical temperatures. In this connection, many equations have been proposed, which relate the variables p, $\underline{v}$ and T and which define the actual dependences more accurately. The most familiar equation is the van der Waals equation of state which makes allowance for the volume occupied by the molecules themselves; in the kinetic ideal gas theory this volume is considered to be negligibly small as compared with the volume of gas. Account is also taken of the attractive forces between the molecules, which depend on the intermolecular distance. If the molecules of a gas are visualized as incompressible, rigid spheres of diameter σ, then, as can be seen from Fig. 1.7, an "excluded volume" of radius σ exists around each molecule and no centre of another molecule can get into this volume. If we denote Avogadro's number by N_A, then the excluded volume per mole will be equal to (4/3) $N_A \pi \sigma^3$ but since two molecules are involved in a collision, the volume which is inaccessible for the free motion of molecules should be considered to be equal to half of that indicated. Thus, the volume accessible for the free motion of the molecules is

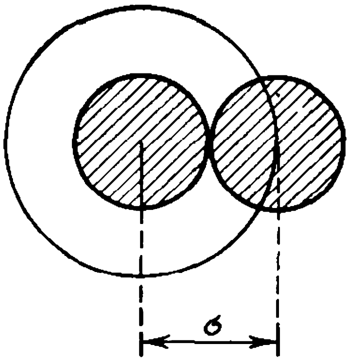

Fig. 1.7. Determination of the excluded volume b according to van der Waals.

$$\underline{v} - b$$

where, as before, $\underline{v}$ is the molar volume of gas and $b = 4\left(\frac{1}{6} N_A \pi \sigma^3\right)$, i.e., is 4 times the volume of a single molecule.

The intermolecular attractive forces (which are still referred to as van der Waals forces) decrease very rapidly with increasing distance between the molecules. In this particular case these forces are considered to be inversely proportional to the sixth power of the distance or to the second power of the volume occupied by the gas. It is also assumed that the attractive forces are on the whole summed up together with the external pressure that holds the gas in the given volume. Thus, the van der Waals equation has the form

$$(\underline{v} - b)\left(p + \frac{a}{\underline{v}^2}\right) = RT \qquad (1.18)$$

or for n moles of substance

$$(V - nb)\left(p + \frac{n^2 a}{V^2}\right) = nRT \qquad (1.19)$$

TABLE 1.3. The Values of the van der Waals Constants for Selected Substances

Substance	a, litre^2 × × atm/mole^2	b, cm^3/mole	Substance	a, litre^2 × × atm/mole^2	b, cm^3/mole
He	0.0340	23.4	Cl_2	5.34	46.0
Ne	0.211	17.1	CO	1.49	39.9
Ar	1.35	2.2	CO_2	3.59	42.7
Kr	2.32	39.8	NO	1.34	27.9
Xe	4.19	51.1	C_2H_4	4.47	57.1
H_2	0.244	26.6	NH_3	4.17	37.1
N_2	1.39	39.1	H_2O	5.72	31.9
O_2	1.36	31.8	Hg	8.09	17.0

Table 1.3 lists the constants a and b for some substances. The term a/V^2, which reflects the intermolecular attraction and which is summed up with the pressure, is called the *internal* or *static pressure*. For liquids it can reach several thousands of atmospheres and for gases it may have different signs. For example, for hydrogen under ordinary conditions the internal pressure is negative, i.e., the repulsive forces operating between the hydrogen molecules exceed the forces of attraction.*

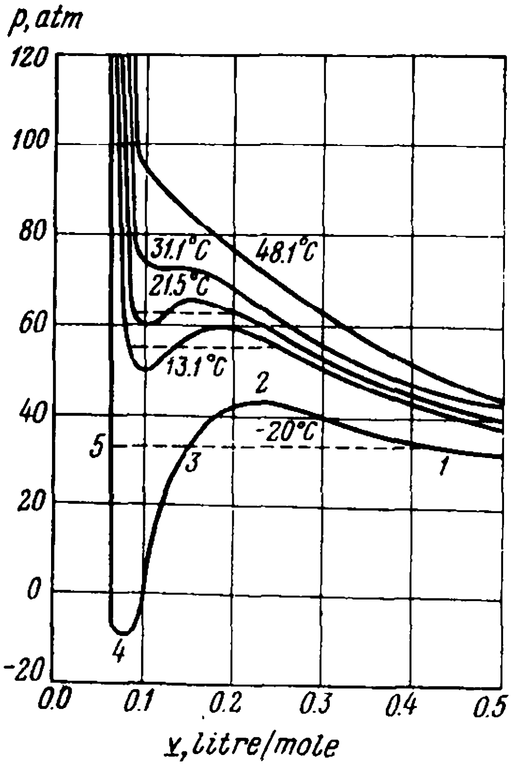

Fig. 1.8. The van der Waals isotherms for carbon dioxide [plotted in accordance with Eq. (1.18) with the following values of the constants: a = 3.59 litre^2 · atm/mole^2; b = 0.0427 litre/mole].

Equation (1.19) contains the volume raised to the third power; hence, it has either three real roots or one real and two imaginary roots. Figure 1.8 shows the curves calculated from the constants a and b for carbon dioxide. At higher temperatures there is one real root and as the temperature increases further the van der Waals curves approach hyperbolas corresponding to the ideal gas equation. However, at temperatures below the critical temperature (t_{cr} = = 31.1°C) no straight horizontal lines corresponding to the equilibrium coexistence of liquid and vapour (a heterogeneous region) are obtained, as shown in Figs. 1.4 and 1.5. Instead, the van der Waals equation gives a wave-like curve (e.g. *12345*) with three real roots, of which only two, namely *1* and *5*, are physically real. The third root (point *3*) is not physically real and lies on the branch of the curve corresponding to the unnatural condition that an increase in pressure produces an increase in volume.

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* The internal or static pressure will be discussed in detail on pp. 126-128.

To bring a theoretical graph into agreement with an experimental equilibrium isotherm (see Fig. 1.4) it is necessary to draw an extra straight horizontal line *15*. According to the rule worked out by Maxwell, which has a theoretical backing, this should be done so that the areas of the figures *1231* and *3453* be equal. Then the ordinate of the straight line *15* will correspond to the saturated vapour pressure at a given temperature and the abscissas of the points *1* and *5* must be equal to the molar volumes of liquid and vapour at the given temperature. Nevertheless, some of the portions of the wave-like curve are physically realizable, though they correspond to non-equilibrium states. For example, by compressing cautiously the vapour above the point *1* (see Fig. 1.8) one can rise along the curve *12*. To do this, it is necessary that no centres of condensation (in the first place, dust) be present in the vapour. The vapour will in this case be found to be in the supersaturated, i.e., supercooled, state. The liquefaction of this vapour can be favoured by ions that appear in the vapour for some reason. This property of supersaturated vapour is made use of in the famous Wilson cloud chamber, which is employed in the investigation of nuclear processes. A fast particle, while passing in the chamber containing supersaturated water vapour and colliding with molecules, forms ions on its path and, as a result, a fog track deposits along the path of the particles which can be photographed.

The portion of the wavy curve *54* is also partly realizable. Here it is necessary to reduce the pressure above the liquid below the supersaturated vapour pressure and no supersaturated vapour must be allowed to form. Some special procedures can be used to produce a liquid in such an "extended" state.

The constants a and b of the van der Waals equation are related to the values of the volume, pressure and temperature. In order to establish this relationship let us rewrite Eq. (1.18) in the form of a cubic equation:

$$\underline{v}^3-\left(b+\frac{RT}{p}\right)\underline{v}^2+\frac{a}{p}\underline{v}-\frac{ab}{p}=0 \qquad (1.20)$$

or in a binomial form:

$$(\underline{v}-\underline{v}_1)(\underline{v}-\underline{v}_2)(\underline{v}-\underline{v}_3)=0 \qquad (1.21)$$

where $\underline{v}_1$, $\underline{v}_2$, $\underline{v}_3$ are the three roots of the cubic equation (1.20). At the critical point all the three roots are equal, i.e., $\underline{v}_1=\underline{v}_2=$

$= \underline{v}_3 = \underline{v}_{cr}$, and Eq. (1 21) can be rewritten in the following form:

$$(\underline{v}-\underline{v}_{cr})^3 = 0$$

or it can be given in an expanded form by raising it to the third power:

$$\underline{v}^3 - 3\underline{v}_{cr}\underline{v}^2 - 3\underline{v}_{cr}^2\underline{v} + \underline{v}_{cr}^3 = 0 \qquad (1.22)$$

Substituting the critical values, $p = p_{cr}$ and $T = T_{cr}$, into the initial equation (1.20) and comparing the coefficients with Eq. (1.22), we find

$$\underline{v}_{cr} = \frac{1}{3}\left(b + \frac{RT_{cr}}{p_{cr}}\right) = \left(\frac{a}{3p_{cr}}\right)^{1/2} = \left(\frac{ab}{p_{cr}}\right)^{1/3} \qquad (1.23)$$

From the last equality we determine the critical pressure:

$$p_{cr} = \frac{a}{27b^2} \qquad (1.24)$$

Through appropriate substitutions we find that

$$\underline{v}_{cr} = 3b \qquad (1.25)$$

and

$$T_{cr} = \frac{8a}{24Rb} \qquad (1.26)$$

But in practice the critical quantities are measured experimentally and the results obtained are used to calculate the constants a and b. In this connection, it is useful to solve relations (1.24), (1.25) and (1.26) for the constants:

$$b = \frac{\underline{v}_{cr}}{3} \qquad (1.27)$$

$$a = 3p_{cr}\underline{v}_{cr}^2 \qquad (1.28)$$

$$R = \frac{8}{3}\,\frac{p_{cr}\underline{v}_{cr}}{T_{cr}} \qquad (1.29)$$

Here the constant R is interpreted in the same manner as are the constants a and b. However, R is in fact the universal gas constant known from the ideal gas law. Since the critical volume is a difficultly determinable quantity, it is expedient to eliminate it from relations (1.27), (1.28) and (1.29). Having done so, we obtain the following expressions for the van der Waals constants:

$$b = \frac{RT_{cr}}{8p_{cr}} \qquad (1.30)$$

and

$$a = \frac{27R^2T_{cr}^2}{64p_{cr}} \qquad (1.31)$$

The values of a and b given in Table 1.3 have been obtained in this way.

If, as has been said, R in Eq. (1.29) is considered to be the universal gas constant, then the relation following from it will be of interest:

$$\frac{RT_{\mathrm{cr}}}{p_{\mathrm{cr}}\underline{v}_{\mathrm{cr}}}=\frac{8}{3}=2.67 \text{ (after van der Waals)} \qquad (1.32)$$

This relation differs significantly from the equality $RT/p\underline{v} = 1$ which follows from the ideal gas equation. However, the number 2.67 is nevertheless substantially less than the average experimental value of the ratio $RT_{\mathrm{cr}}/p_{\mathrm{cr}}\underline{v}_{\mathrm{cr}}$ equal to 3.75.

Of definite interest is the van der Waals equation in the so-called *reduced form*. We replace the constants a, b and R in the original equation (1.18) by expressions (1.27), (1.28) and (1.29) through the critical quantities:

$$\left(p+\frac{3p_{\mathrm{cr}}\underline{v}_{\mathrm{cr}}^{2}}{\underline{v}^{2}}\right)\left(\underline{v}-\frac{\underline{v}_{\mathrm{cr}}}{3}\right)=\frac{8}{3}\,\frac{p_{\mathrm{cr}}\underline{v}_{\mathrm{cr}}}{T_{\mathrm{cr}}}\,T \qquad (1.33)$$

After dividing by $p_{\mathrm{cr}}\underline{v}_{\mathrm{cr}}$ and multiplying by 3 Eq. (1.33) can be written as a function of the following relations:

$$\pi=\frac{p}{p_{\mathrm{cr}}};\ \varphi=\frac{v}{v_{\mathrm{cr}}} \text{ and } \tau=\frac{T}{T_{\mathrm{cr}}} \qquad (1.34)$$

which are called, respectively, the *reduced pressure*, the *reduced volume* and the *reduced temperature*, namely:

$$\left(\pi+\frac{3}{\varphi^{2}}\right)(3\varphi-1)=8\tau \qquad (1.35)$$

This equation is known as the reduced van der Waals equation of state. It is one of the manifestations of the more general principle of corresponding states (van der Waals, 1881)—the postulate as to the existence of a universal equation of state written in terms of reduced variables. Indeed, since the reduced equation does not contain the individual constants in an explicit form, it can be applied to any substance. Of course, this equation contains implicitly the individual characteristics of a substance—in terms of the critical quantities. Thus, Eq. (1.35) is a special case (an approximate realization) of the universal reduced equation of state in a general form

$$F(\pi,\varphi,\tau)=0 \qquad (1.36)$$

the assumption of whose existence is in itself an approximation.

As can be shown, any equation of state that contains three parameters can be presented in the reduced form (1.36). The *Dieterici equation of state* is an equation of this kind:

$$p(\underline{v}-b)=RTe^{-A/RT\underline{v}} \qquad (1.37)$$

This equation is more accurate than the van der Waals equation, though more complicated. In Eq. (1.37) the constant b has the same meaning as in the van der Waals equation, a new constant A appears and the constant a is missing. The reduced form of the Dieterici equation of state has the form

$$\pi(2\varphi-1)\exp\left(\frac{2}{\tau\varphi}-2\right)=\tau \tag{1.38}$$

where π, φ and τ have been defined by (1.34). According to the Dieterici equation of state the ratio

$$\frac{RT_{\text{cr}}}{p_{\text{cr}}\underline{v}_{\text{cr}}}=\frac{e^2}{2}=3.695 \text{ (after Dieterici)} \tag{1.39}$$

which agrees much better with the average experimental value 3.75 than the one following from the van der Waals equation.

Comparatively more precise equations of state are those containing more than three constants, say the Beattie-Bridgman equation

$$p=\frac{R'(\underline{v}+B)}{\underline{v}^2}-\frac{A}{\underline{v}^2} \tag{1.40}$$

where

$$A=A_0\left(1-\frac{a}{\underline{v}}\right);\ B=B_0\left(1-\frac{b}{\underline{v}}\right);\ R'=R\left(1-\frac{c}{\underline{v}T^3}\right) \tag{1.41}$$

Apart from R, this equation contains five empirical constants, A_0, B_0, a, b and c and is considered to be one of the best empirical equations of state, the total number of equations of state amounting to about 150. It is capable of describing experimental p-v-T data with an accuracy of up to 0.5 per cent, including the critical region.

Equations of State with Virial Coefficients. The behaviour of a real gas can be described with any degree of accuracy with the aid of the equation which was proposed in 1901 by Kammerlingh Onnes* and which is known as *an equation of state with virial*** *coefficients* or a *virial equation*:

$$p\underline{v}=RT+b(T)p+c(T)p^2+\dots \tag{1.42}$$

This equation is also written in a somewhat different form:

$$p\underline{v}=RT\left[1+\frac{B(T)}{\underline{v}}+\frac{C(T)}{\underline{v}^2}+\dots\right] \tag{1.43}$$

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* More exactly, Kammerlingh Onnes proposed the "Leiden form" of Eq. (1.43) and the "Berlin form" (1.42) was proposed by Holborn.

** The name is associated with the fact that the equation of state of a real gas in this form can be deduced with the aid of the virial theorem of Clausius (1870) and of some simplifying assumptions concerning the law of the forces of intermolecular interactions.

It can be shown that the consideration of a real gas by means of methods of statistical mechanics (see Chapter 6) leads to an equation of state in the form of a virial expansion of the type (1.42) or (1.43). The temperature functions $b(T)$, $c(T)$, ..., or $B(T)$, $C(T)$, ... are called, respectively, the second, third, etc., virial coefficients. The first virial coefficient is equal to unity in accordance with Eq. (1.43).

The relationship between the various types of virial coefficients can be deduced as follows. Let us write Eq. (1.43) in the form

$$p=\frac{RT}{\underline{v}}+\frac{RTB(T)}{\underline{v}^2}+\cdots \tag{1.44}$$

Further we introduce this expression for p into Eq. (1.42), retaining only the first two terms of the expansion; we obtain

$$p\underline{v}=RT+b(T)\left[\frac{RT}{\underline{v}}+\frac{RTB(T)}{\underline{v}^2}\right]+c(T)\left(\frac{RT}{\underline{v}}\right)^2+\cdots \tag{1.45}$$

Comparing the last expression with Eq. (1.43), we see that the second virial coefficients are equal, i.e.,

$$b(T)=B(T) \tag{1.46}$$

As regards the third coefficients, they are connected by a more complex relation:

$$c(T)=\frac{C(T)-b(T)B(T)}{RT}=\frac{C(T)-B^2(T)}{RT} \tag{1.47}$$

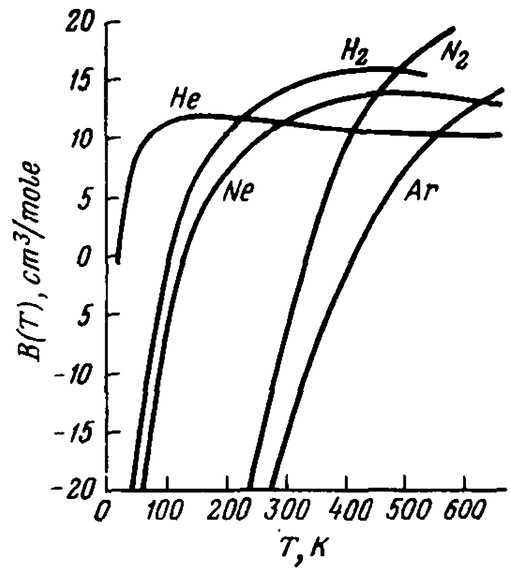

Fig. 1.9. Temperature dependence of second virial coefficients for some gases.

Figure 1.9 shows the dependence of the second virial coefficient $b(T)$ on temperature for a few gases. The temperature at which $b(T)=0$ is called the *Boyle temperature*. The meaning of the term can be explained in the following way. Let us write Eq. (1.42) as the pressure dependence of the compressibility factor (also known as the compression factor)

$$Z=\frac{p\underline{v}}{RT} \tag{1.48}$$

which is equal to unity for an ideal gas:

$$Z=\frac{p\underline{v}}{RT}=1+\frac{b(T)}{RT}p+\frac{c(T)}{RT}p^2+\cdots \tag{1.49}$$

Further we differentiate Z with respect to the pressure at constant temperature:

$$\left(\frac{\partial Z}{\partial p}\right)_T=\frac{b\,(T)}{RT}+\frac{2c\,(T)}{RT}\,p+\ldots \tag{1.50}$$

The initial slope of the isothermal curve of Z versus p will be expressed by the following relation:

$$\left[\left(\frac{\partial Z}{\partial p}\right)_T\right]_{p\to 0}=\frac{b\,(T)}{RT} \tag{1.51}$$

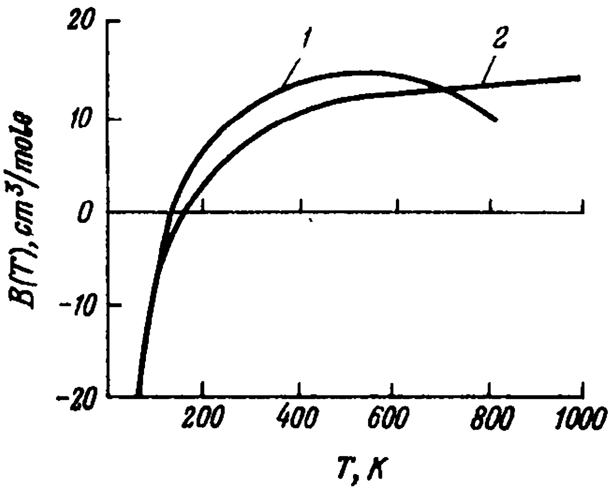

Fig. 1.10. The second virial coefficient for neon, found experimentally (1) and calculated according to the van der Waals equation from relation (1.53) (2) with the following values of the constants: $a = 0.211$ litre²·atm/mole² and $b = 0.0171$ litre/mole [the Boyle temperature at which $B\,(T) = 0$, according to (1.55), is equal to 150 K, whereas experiment shows 134°K].

This quantity vanishes at the Boyle temperature T_B, i.e., at $T = T_B$, when, by definition, $b\,(T) = 0$. Thus,

$$\left[\left(\frac{\partial Z}{\partial p}\right)_T\right]_{p\to 0,\;T=T_B}=\frac{b\,(T_B)}{RT}=0 \tag{1.52}$$

that is, the compressibility factor Z at the Boyle temperature is independent of the pressure, as must be the case for a gas obeying Boyle's law: $p\underline{v} =$ const. From Fig. 1.9 it is seen that at temperatures below T_B the second virial coefficient is negative, and above the Boyle temperature it is positive. At high temperatures $b\,(T)$ and all the virial coefficients of higher ranks tend to zero, and the behaviour of the gas tends to that of an ideal gas.

The second virial coefficient can be related to the constants a and b of the van der Waals equation (1.18). It is precisely the second virial coefficient and not any other:

$$B\,(T)=b\,(T)=b-\frac{a}{RT} \tag{1.53}$$

At the same time, virial coefficients of a higher rank ($n \geqslant 3$) are simply equal to b^{n-1}. For example,

$$C\,(T) = b^2 \tag{1.54}$$

Figure 1.10 gives the values of the second virial coefficients for neon [the experimental values are the same as in Fig. 1.9, i.e., those calculated from relation (1.53)]. As seen, the van der Waals equation describes the temperature dependence $B(T)$ semiqualitatively. According to this equation, the second virial coefficient is negative at low temperatures, passes through zero as the temperature increases and tends to the limit equal to b. The van der Waals equation, however, does not describe the further decrease in $B(T)$ at even higher temperatures and does not allow one to find the correct limiting value at $T \to \infty$. The van der Waals equation is not suitable at all for the determination of the third virial coefficient and also virial coefficients of higher rank.

According to Eqs. (1.52) and (1.53) it is possible to find an expression for the Boyle temperature corresponding to the van der Waals equation:

$$T_B = \frac{a}{Rb} \tag{1.55}$$

Comparing the last relation with Eq. (1.26), we obtain

$$\frac{T_B}{T_{cr}} = \frac{27}{8} = 3.375 \text{ (after van der Waals)} \tag{1.56}$$

This value can be compared with actual data for various gases: He—3.65; H_2—3.21; Ar—2.73; N_2—2.56; NH_3—2.13; CH_4—2.58.

In concluding this section we shall dwell in more detail on the characteristics of single-phase systems and on some relationships associated with the extensive and intensive properties of the system. Extensive properties include the volume. Let V be the volume of a one-phase system containing $n_1, n_2, \ldots, n_e$ moles of different substances—the components of the system. The phase is homogeneous by definition. If we pick out a part k, then the volume kV will evidently contain kn_i of each ith component. Here k may be an arbitrary positive integer. We choose temperature and pressure as the main properties and write the state equation of the system:

$$V = V(T, p, n_1, n_2, \ldots, n_e) \tag{1.57}$$

which expresses the dependence of the volume on the independent variables $T, p, n_1, n_2, \ldots, n_e$. In view of what has been said above, we can write the function (1.57) in a different form:

$$V(T, p, kn_1, kn_2, \ldots, kn_e) = kV \tag{1.58}$$

and this means that at the same temperature and pressure the system containing the components in the amounts $kn_1, kn_2, \ldots, kn_e$ will occupy the volume kV, i.e., the volume which differs by k times from the initial volume. Rewriting Eq. (1.58) in a more expanded form

$$V(T, p, kn_1, kn_2, \ldots, kn_e) = kV\,(T, p, n_1, n_2, \ldots, n_e) \tag{1.59}$$

we obtain a relation from which it follows that the volume of a homogeneous system and any other extensive property is a *homo-*

geneous function of first degree in the number of moles of the components.

We shall now formulate the general theorem on homogeneous functions. Thus, the function $f(x, y, z \ldots)$ is said to be homogeneous of degree m in the variables $x, y, z, \ldots$, if the following identity holds:

$$f(kx, ky, kz \ldots) = k^m f(x, y, z \ldots) \tag{1.60}$$

Differentiating Eq. (1.60) with respect to k, we obtain:

$$\frac{\partial f(kx, ky, kz \ldots)}{\partial (kx)} x + \frac{\partial f(kx, ky, kz \ldots)}{\partial (ky)} y + \\ + \frac{\partial f(kx, ky, kz \ldots)}{\partial (kz)} z + \ldots = mk^{m-1} f(x, y, z \ldots) \tag{1.61}$$

In a special case it may be assumed that $k = 1$, in which case Euler's theorem on homogeneous functions of mth degree is obtained:

$$\frac{\partial f}{\partial x} x + \frac{\partial f}{\partial y} y + \frac{\partial f}{\partial z} z + \ldots = mf(x, y, z \ldots) \tag{1.62}$$

The converse is also true: any function that satisfies this condition is a homogeneous function of mth degree.

In thermodynamics one deals mainly with two simplest cases. First, with functions of first degree ($m = 1$) when

$$f(kx, ky, kz \ldots) = kf(x, y, z \ldots) \tag{1.63}$$

and Eq. (1.62) has the following form for c independent variables:

$$\sum_{r=1}^{c} \frac{\partial f}{\partial r} r = f(x, y, z \ldots) \quad (r = 1, 2, \ldots, c) \tag{1.64}$$

Second, of substantial importance in thermodynamics are homogeneous functions of degree zero ($m = 0$) when

$$f(kx, ky, kz, \ldots) = f(x, y, z, \ldots)$$

and

$$\sum_{r=1}^{c} \frac{\partial f}{\partial r} r = 0 \quad (r = 1, 2, \ldots, c) \tag{1.65}$$

From the foregoing it follows that the volume of a homogeneous system is a homogeneous function of first degree with respect to the independent variables $n_1, n_2, \ldots, n_c$. Hence, according to Eq. (1.64) the following identity must hold:

$$\sum_{i=1}^{c} \left[\frac{\partial V(T, p, n_1, n_2, \ldots, n_c)}{\partial n_i}\right]_{T, p, n_j \neq n_i} n_i = V(T, p, n_1, n_2, \ldots, n_c) \tag{1.66}$$

Differentiating Eq. (1.66) with respect to n_j, where j is one of the indices 1, ..., c, then for each j we get

$$\sum_i \frac{\partial^2 V}{\partial n_i \, \partial n_j} n_i + \frac{\partial V}{\partial n_j} \equiv \frac{\partial V}{\partial n_j} \qquad (1.67)$$

or

$$\sum_i \frac{\partial^2 V}{\partial n_i \, \partial n_j} n_i = 0 \qquad (1.68)$$

These equations can be simplified if we introduce the important concept of the *partial molar volume* of a component of a homogeneous mixture:

$$\bar{v}_i \equiv \left(\frac{\partial V}{\partial n_i}\right)_{T,\, p,\, n_j \neq n_i} \qquad (1.69)$$

Here it should be kept in mind that the partial molar volume is only a spectacular example of the partial molar values of the extensive properties of the system—energy, entropy, etc. The value of $\bar{v}_i$ is, as it were, the contribution of a given component to the total volume of the system. The significance of this quantity can be understood if we imagine a very large amount of the mixture (a phase) to which is added one mole of the ith component at constant temperature and pressure. The change in the volume of the system that occurs is exactly the partial molar volume of the given component. In contrast to the ordinary volume, say the molar volume v, the volume $\bar{v}_i$ may be positive, negative, or equal to zero. Thus, for example, when $MgSO_4$ is added to a dilute solution of this salt, the volume decreases and, hence, $\bar{v}_i < 0$.

Using the notation (1.69), we can express, on the basis of Euler's theorem, the total volume of a single-phase system as the sum of the partial molar volumes:

$$V = n_1\bar{v}_1 + n_2\bar{v}_2 + \ldots + n_c\bar{v}_c = \sum_{i=1}^{c} n_i\bar{v}_i \qquad (1.70)$$

What has been said above applies equally well to the other extensive properties of the system.

On the other hand, the sum of the second derivatives of the volume written in the form (1.68) may be represented as follows:

$$\sum \left(\frac{\partial v_i}{\partial n_j}\right)_{\substack{n_j \\ T,\, p\ldots}} = 0 \quad \text{or} \quad \sum \left(\frac{\partial v_j}{\partial n_i}\right)_{\substack{n_j \\ T,\, p\ldots}} = 0 \qquad (1.71)$$

This means that the partial molar volumes satisfy relation (1.65) and are homogeneous function of zeroth degree in the variables

n_1, n_2, ..., n_c. For all the components we can write:

$$\bar{v}_i (T, p, kn_1, kn_2, \ldots, kn_c) = \bar{v}_i (T, p, n_1, n_2, \ldots, n_c) \quad (1.72)$$

Thus, all the numbers of moles and, hence, the total volume of the system are changed k times and the value of $\bar{v}_i$ does not change. This is characteristic of the intensive quantities, i.e., of the intensive properties of the system; these quantities also include temperature and pressure. Hence, the partial molar volumes $\bar{v}_i$, just as the partial molar values of the extensive properties Y in general, determinable by the derivative

$$\bar{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T, p, n_j \neq n_i} \quad (1.73)$$

are *intensive quantities*. Let us consider a mixture of ideal gases containing n_1, n_2, ..., n_c moles of the components. The total volume of the system

$$V = \frac{nRT}{p} = (n_1 + n_2 + \ldots + n_c) \frac{RT}{p}$$

depends on T and p and is a homogeneous function of first degree expressed in terms of n_1, n_2, ..., n_c. On the other hand, the partial molar volume

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T, p, n_j \neq n_i} = \frac{RT}{p}$$

is the same for all the components and is independent of n_i, being an intensive property.

It should be added that for a one-component system (a pure substance) the partial molar value of this or that extensive property coincides with the molar value of the property, i.e.,

$$\bar{Y}_i = \frac{Y}{n} = \underline{Y} \quad (1.74)$$

where n is the number of moles of the substance. Thus, the assignment of a given extensive property (the volume, energy, etc.) to unit mass leads to an intensive quantity. The methods of experimental determination of partial molar quantities (the volume) are considered in Chapter 7 (Sec. 7.2).

A multicomponent system may also undergo changes in the numbers of moles of the components brought about by chemical reactions. Suppose that a single reaction takes place in the system which is described by the stoichiometric equation

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightarrow \nu_1' B_1' + \nu_2' B_2' + \ldots \quad (1.75)$$

Suppose the numbers of moles of the participants in the reaction have been changed, respectively, by the following amounts: dn_1,

$dn_2, \ldots, dn'_1, dn'_2, \ldots$. Then we can write the following equality in accordance with Eq. (1.75):

$$\frac{dn_1}{-\nu_1} = \frac{dn_2}{-\nu_2} = \ldots = \frac{dn'_1}{\nu'_1} = \frac{dn'_2}{\nu'_2} = \ldots \equiv d\xi \qquad (1.76)$$

thereby determining the change, in the system, of a *chemical variable* ξ which is called the *extent of reaction* or the *reaction coordinate.* Thus, when $\Delta\xi = 1$, it is said that one equivalent of reaction has occurred.

In what follows the change in volume, for example, that occurs in a closed system with the specified initial numbers of moles n_1^0, $n_2^0, \ldots$, can be expressed in terms of the chemical variable. For example, instead of

$$v = v\,(T, p, n_1, n_2, \ldots, n_c) \qquad (1.77)$$

we can write

$$v = v\,(T, p, \xi, n_1^0, n_2^0, \ldots, n_c^0) \qquad (1.78)$$

or for a system with given initial numbers of moles we can write the dependence of the volume in a more abbreviated form:

$$v = v\,(T, p, \xi) \quad \text{(one reaction)} \qquad (1.79)$$

Similar functions can also be written for other extensive properties of the system.

Generally speaking, any changes in the system occur in time, and if the chemical variable in a homogeneous system has changed by $d\xi$ in time dt, then, according to de Donder (1930), the relation

$$\frac{d\xi}{dt} \equiv w$$

is called the reaction rate for the entire system.*

1.3. Energy, Work and Heat

The concept of the quantity characterizing the motion and having, according to modern terminology, the dimensions of "energy" was first developed in mechanics. The founders were Galilei (1564-1642), Huygens (1629-1695) and Newton (1642-1727). According to these scientists, when a body of mass m falls from height h, the acceleration due to gravity being g, the decrease in the potential energy of the body (its gravitational energy) mgh is equal to an increment in its kinetic energy $mv^2/2$. Until the middle of the 19th century the law of conservation of energy seemed to be a special case realizable in "pure mechanics" in the absence of friction. The term itself, "energy", was invented by Clausius (1864) who was the first to introduce the term into physics. Before Clausius the term "force" had been used instead of "energy" for quantities having different dimensions. Helmholtz wrote an article devoted to the law of conservation of energy and entitled it "On the conservation of force" (1847). Incidentally, according to Newton, force is the cause of motion which performs work ($F \cdot ds \cdot \cos \alpha$) along a certain path, imparting an energy to the body. Thus, the concept of energy is inseparably associated with another concept of the same dimensionality, the work. According to Engels, "Work ... is change of form of motion regarded in its quantitative aspect".* The most difficult task was the establishment of the general law of conservation of energy, including the action of dissipative forces leading to the dissipation of work and its conversion into heat.

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* In contrast to the reaction rate per unit volume.

The earliest concept of heat was undoubtedly physiological, that is, based on the sensations of hot and cold. But Black (1759) was evidently the first to succeed in differentiating between temperature as a measure of the extent to which a body is heated and heat, the amount of which determines the extent of heating for the given body. Black, whose lectures read at the University in Glasgo were published (after the author had died), also established at the beginning of the 19th century the dependence of the extent of heating on the properties of the body, i.e., introduced the concept of heat capacity. It was clear to Black that the transfer of heat from one body to another occurs only when there is a difference in temperature and also that two bodies in a state of thermal equilibrium must have equal temperatures. The latter proposition, which is the condition of thermal equilibrium, was not quite clear even to Faraday who thought, on the basis of inaccurate measurements, that the temperature of the vapour over a boiling solution was equal to the boiling temperature of the solvent, i.e., differed from the temperature of the solution.

Originally, a separate law of conservation was adopted for heat since it was thought to be an elastic, weightless and indestructible fluid which could be perceptible as well as latent (Clegghorn, 1774). This fluid was termed the thermogen. Benjamin Thompson (1753-1814), who is also known as Count Rumford, was evidently the first to make a break in the then widespread popular theory of the thermogen. First, he showed, within the weighing accuracy possible at the time, that the thermogen, if there is one, must be weightless. Second, while observing the boring of cannon, he came to the fundamental conclusion as to the proportionality between the amount of heat evolved on boring and the work expended. Thus, the dissipative forces that convert work into heat were introduced into the orbit of the law being worked out. A further step was made by Julius Robert von Mayer (1814-1878), who established the mechanical equivalent of heat and formulated in 1842, on the basis of physiological observations, the law of interconversion of qualitatively different natural forces (kinds of energy). These conversions are accomplished, according to Mayer, within definite equivalent ratios. About that time James Prescott Joule enunciated the equivalency of mechanical work and electric power (energy) and the heat produced. This was followed by the publication of H. von Helmholtz's paper "On the conservation of force" (1847) devoted to the law of conservation of energy. Finally, the term energy appeared in the works of William Thomson and Rudolf Clausius (1864). Mention should also be made of the work of Maxwell "The Theory of Heat" (1871). This culminated the stage in the development of physics which is characterized, as was expressed much later by Einstein, "by the tendency towards reducing a multitude of phenomena to a purely theoretical system composed of the smallest number of elements possible".* Indeed, a single "element", energy, unites an extremely large variety of phenomena and the law of conservation of energy involves no exceptions either in the macro- or in the microworld. Nonetheless, it is necessary to adopt some definition of energy. Engels wrote: "... matter is unthinkable without motion. And if, in addition, matter confronts us as something given, equally uncreatable as indestructible, it follows that motion also is as uncreatable as indestructible."** According to Engels, energy is a measure of motion upon transformation of one kind of motion into another. This definition is in agreement with the definition given by a physicist, Max Planck: "The energy of a material system in a certain state is defined as a quantity measured in mechanical units of work, which embraces all the operations that are performed outside the system when the latter is transformed in some way from a given state to an arbitrarily fixed zeroth state."*** Here it is meant that the actions, i.e., the changes that occur in nature as a result of the process of interest taking place in our system, have a mechanical equivalent in the form of the amount of work *into which this action can be converted*, or the amount of work, *the consumption of which is minimally required to perform the given action.*

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* Engels, F., *Dialectics of Nature*, Progress Publishers, Moscow, 1972.

The above definition of energy becomes physically real provided the law of conservation of energy is formulated, for example, as follows: "The energy of a material system in a certain definite state taken relative to another definite 'zeroth' state has a unique value.****

Thus, the energy of the system is its inherent property (or its state variable) and its changes associated with the above-mentioned actions performed over other systems (the outside environment) cause changes in the energy of these other systems, and these changes in turn can be expressed in the equivalent of mechanical work.

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* Einstein, A., *Ideas and Opinions*, New York, 1954.

** Engels, F., *Dialectics of Nature*, Progress Publishers, Moscow, 1972.

*** Planck, M., *Das Prinzip der Erhaltung der Energy*, Leipzig, Berlin, 1921.

**** Ibid.

Considering the unambiguity of the value of energy of the system in regard to the "zeroth" state, we may speak of the "reserve" or "content" of the energy in the system. In this connection, it is necessary to consider the concepts of work and heat, the quantities which have the dimensions of energy but are far from being equivalent to it. The concept of work (mechanical work, say, the lifting of a weight or the compression of a spring) is, as has already been said, the most distinct measure of energy. But could one speak of work as the quantity stored by the system, i.e., as a property of the system? We cannot do so since when speaking of work one implies a process in which one system performs work on another system (for example, a gas while expanding in a cylinder with a piston can compress a spring and thereby impart some of its energy to it). Hence, work is one of the forms of transfer of energy from one system to another. Emphasis should be placed here on the macroscopic nature of the transfer of energy in the form of work and the ideally possible complete reversibility of this transfer.

Another form of transfer of energy from one system to another is heat which cannot be regarded either as a certain reserve, i.e., as a property inherent in the system in a given state. The widespread definition of heat as the molecular-kinetic energy of a body is erroneous. Thus, for example, the latent heat given off by a system upon condensation of vapour is due mainly to the loss of the potential energy of molecular interaction. Nonetheless, when the energy is transferred in the form of heat, the system receives it in a micromolecular form, i.e., in the form of motion and molecular interaction.

Thus, work is a macrophysical form of transfer of energy, and heat is a microphysical form. According to the second law of thermodynamics, these forms are not equivalent and if in some process work is converted into heat (say, by way of friction), then such a conversion is unlimited. The reverse conversion, that of heat into work, is limited by certain conditions.

Here we have made use of the microphysical concepts in order to account for the difference between heat and work; they lie beyond the scope of phenomenological thermodynamics. Within this framework the non-equivalency of the modes of transfer of energy in the form of work and heat is established, as has just been mentioned, by one of the most fundamental law of natural science—the second law of thermodynamics (see Chapter 3).

Chapter 2

The Zeroth and First Laws of Thermodynamics

2.1. Equilibrium. The Zeroth Law of Thermodynamics

Let us consider an arbitrary system and assume that its intensive properties do not change in time. This is possible in two cases which differ in behaviour of the system after it is insulated against any influences. Suppose that the system is completely isolated from the environment (by placing it in a special container or by building walls, etc.). If in this case too nothing happens to the system and its intensive properties continue to be unaltered, then we say that the system is in the *state of equilibrium*.

On the other hand, if after being isolated the system has undergone changes, then it means that before the isolation it was in a *steady state* in which the constancy of the intensive properties is retained owing to the action of some external factors. Steady states are studied by the methods of non-equilibrium or irreversible thermodynamics (see Chapter 9). An example is given in Chapter 9 (see page 420) where a mixture of nitrogen and oxygen placed in a vessel is kept in a partly separated state owing to a constant temperature difference. If such a system is isolated from external heat sources, the temperature difference will disappear and the composition of the gas mixture will be the same throughout the entire volume. The system is then said to have been brought into a state of *internal equilibrium*.

In connection with the difference drawn above between equilibrium and steady states it should be mentioned here that there exist two sections of thermodynamics, namely the thermodynamics of equilibrium states (and processes) or classical thermodynamics and the thermodynamics of non-equilibrium (or irreversible) processes.

As has already been said, a "thermodynamic system" is separated from its surroundings by real or imaginary boundaries. If these boundaries do not permit the transfer of matter to or from the surroundings, they are called *walls*. The walls can have various properties. For example, they may be *rigid*, i.e., non-deformable, so that the volume of the system, enclosed by such walls, remains constant. Also, the walls may be or, in principle, may not be *heat-conducting*. What does it mean? Suppose we have two systems, each of which is in a state of internal equilibrium and is surrounded by rigid walls of some kind. Initially, these systems are separated and are not in equilibrium with each other. However, when they are brought into contact with each other, the state of each of the systems undergoes changes until a new state is reached, which will not change with time. Such rigid walls are called heat-conducting. The final state of mutual equilibrium attained through thermal contact is called *thermal equilibrium.*

The problems pertaining to thermal equilibrium were examined as early as the second half of the 19th century by J. Black. However, not everything was clear at the time. Even the great Faraday wrote in 1822 an article for the journal edited by Gay-Lussac in which he pointed out that the temperature of the boiling solution of a nonvolatile substance was not equal to the temperature of the vapour in equilibrium with it. Namely, the temperature of the vapour above the boiling solution is lower and equal, as has already been mentioned, to the boiling temperature of the solvent. In actual fact, this is not so: the temperature of the vapour in equilibrium with the boiling solution is equal to the boiling temperature of the solution. If, however, an ordinary thermometer is held above the solution, the vapour will be condensed on it due to the incomplete thermal insulation and the considerable heat capacity of the thermometer itself, i.e., the pure solvent will appear and the thermometer will indicate the boiling temperature of the solvent.

Courses of thermodynamics usually deal with three laws: the first, second and third laws, which constitute the subject matter of thermodynamics. However, at present an ever increasing use is made in thermodynamics of the law of thermal equilibrium formulated by R. Fowler in 1931, i.e., much later than the basic laws were established. Since it was not thought to be reasonable to embark on the long-standing, traditional enumeration of the basic principles, the new law was termed the zeroth law of thermodynamics. This law states: *if two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.* At first glance, this proposition may seem quite obvious and even trivial. But this is not so, in fact. This law cannot be applied, for example, to chemical equilibrium. For example, ammonia (system I) and hydrogen chloride (system II) can be in equilibrium with nitrogen (system III). But, as known, they will react rapidly with each other.

The zeroth law leads us to an analytical criterion of thermal equilibrium determined by the equality of a certain property of systems identified with temperature.

Let us consider three systems capable of exchanging energy in the form of heat. Suppose that each of the three systems is characterized by a certain number of variables, i.e., properties that specify its state. We shall confine ourselves to a special case where it will suffice to consider only two variables, say the pressure p and the volume v. If two systems can interact thermally, then the properties of each of them will be changed. The establishment of a thermal equilibrium between two systems will therefore be associated with the interdependent change of four variables characterizing their state. Mathematically this corresponds to a functional relationship between the four variables. For example, for systems I and II this can be expressed as follows:

$$F(p_1, v_1, p_2, v_2) = 0 \tag{2.1}$$

Analogously, if systems II and III are in thermal equilibrium,

$$G(p_2, v_2, p_3, v_3) = 0 \tag{2.2}$$

Further, according to the zeroth law systems I and III must also be in thermal equilibrium, i.e.,

$$H(p_1, v_1, p_3, v_3) = 0 \tag{2.3}$$

Since all the variables are interconnected, relation (2.3) must be derived from (2.1) and (2.2). But since Eq. (2.3) does not contain the variables p_2 and v_2, then one must find a possibility to eliminate them from Eqs. (2.1) and (2.2). However, only one variable may be eliminated; two variables are eliminated if they are present in a combination as certain functions, say $y\ (p_2, v_2)$, in both equations, (2.1) and (2.2). Analogously, p_1 and v_1 must appear in Eqs. (2.1) and (2.3) in the form of the function $x\ (p_1, v_1)$, whereas p_3 and v_3 form the function $z\ (p_3, v_3)$ in Eqs. (2.2) and (2.3). Therefore, Eqs. (2.1), (2.2) and (2.3) can be written in the form:

$$F(x, y) = 0 \tag{2.4}$$
$$G(y, z) = 0 \tag{2.5}$$
$$H(x, z) = 0 \tag{2.6}$$

It is now possible, in principle, to eliminate any one of the three variables in any two of these equations. For instance, Eqs. (2.5) and (2.6) can be solved for Z, in which case we obtain $Z = X\ (x)$ and $Z = Y\ (y)$. Thus, $X\ (x) = Y\ (y)$, where x is a function of p_1 and v_1 and y is a function of p_2 and v_2. Hence, there must exist functions such as $f_1\ (p_1, v_1)$ and $f_2\ (p_2, v_2)$ so that when system (I) and (II) are in thermal equilibrium, the following equality will hold:

$$f_1\ (p_1, v_1) = f_2\ (p_2, v_2)$$

If another pair of equations are used in an analogous way, say Eqs. (2.4) and (2.5), then we can write the equality of three functions:

$$f_1\ (p_1, v_1) = f_2\ (p_2, v_2) = f_3\ (p_3, v_3)$$

from which we can infer that there exists such a function of the variable properties of the system

$$T = T\ (p, v) \tag{2.7}$$

that any two systems in thermal equilibrium are characterized by the same values of T. This property describes the thermodynamic system from the viewpoint of hot and cold and it may be identified with a certain temperature scale by choosing it so that it coincides with the ideal-gas and thermodynamic scales. In this way the concept of *temperature* can be introduced.

It should be noted that the zeroth law of thermodynamics asserts the existence of an equation of state since relation (2.7) is formally equivalent to the equation

$$F(p, v, T) = 0 \tag{2.8}$$

However, one cannot finalize the form of this function by means of a purely thermodynamic treatment. To achieve this, one must resort to experimental data or to a theoretical consideration of intermolecular interactions, which is what has been done in Chapter 1 with the help of the van der Waals model.

2.2. The Work of a Process

As has already been said, when a system is undergoing a change, i.e., when a process is being accomplished, it can overcome the external forces acting on it and do work. Most frequently the system is acted on by the forces of external pressure. When work is done, the volume of the system increases. Suppose we have a cylinder which contains a gas and is closed by a piston. The piston is loaded and it creates a pressure p. The gas is expanded, say, as a result of heating and moves the piston a distance dl (Fig. 2.1). Since the total force applied to the piston is pS (where S is the surface area of the piston), the element of work being done will be expressed as follows:

$$\delta W_1 = pS\,dl = p\,dv \tag{2.9}$$

that is, will be equal to the product of the pressure and the increase in the volume. With a finite change in volume from v_1 to v_2 the elements of work should be summed over the elements of path, i.e., the following integral should be used:

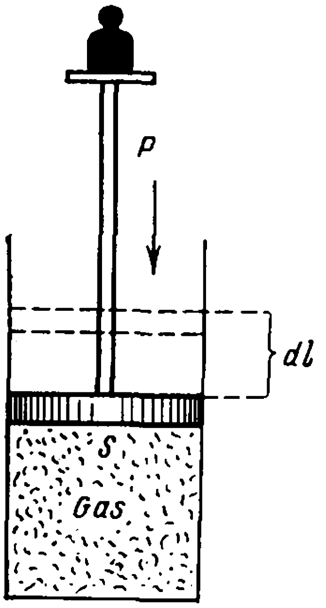

Fig. 2.1. Calculating the work of expansion, $\delta W_1 = pSdl = p\,dv$.

$$W_1 = \int_1^2 \delta W_1 = \int_1^2 p\,dv \tag{2.10}$$

In order to evaluate the integral it is necessary to know the dependence of the pressure on the volume. Some relevant calculations are given in Sec. 2.4.

The pressure is not, generally speaking, the only force acting on the system. For example, there are always present the forces of surface tension γ. The work is in this case associated with the change in the surface of the system, i.e.,*

$$\delta W_2 = -\gamma dO \tag{2.11}$$

This component of the total work plays an essential part in disperse and colloidal systems when the specific surfaces and their possible changes are considerable. The system may also be subjected to electrical forces measured by the potential difference E. Electrical work is equal to the product of E by the quantity of electricity transferred, $d\eta$, i.e.,

$$\delta W_3 = E d\eta \tag{2.12}$$

In a general form the work of a thermodynamic system may be written as the product of a certain generalized force X by the change in the generalized coordinate dx. Thus, the work done by the system is generally a complex quantity; it is expressed by the sum

$$\delta W = p\,dv + \gamma\,dO + E d\eta + X\,dx + \ldots \tag{2.13}$$

where each of the terms is the product of a certain intensive property (an intensity factor) by the increase in the corresponding extensive property (a capacity factor).

In the following discussion we shall simplify the matters by considering systems which are acted only by external forces. Other forces will be considered either to be absent (say, electrical forces, with the exception of galvanic cells) or to be negligibly small, say surface tension in ordinary (non-colloidal) chemical systems. The total work will then be expressed by relation (2.9).

2.3. The First Law of Thermodynamics

The first law of thermodynamics is in essence the law of conservation of energy**, the various formulations of which have been given above.

In order to approach a particular formulation of the law of conservation of energy termed the *first law of thermodynamics* let us consider a closed system which is at internal equilibrium and is completely surrounded by *heat-insulating walls*, i.e., when the system is surrounded by walls such that no changes can be produced in it, except that the system may do work (on its outside environment) or may have work done upon it. The system is called in this case a *heat-insulated system* and any change in state of such a system is termed an *adiabatic process*. Let external forces perform work W_{ad} on such a heat-insulated system. According to the first law (its first part), this work is equal to the increase in a certain extensive property of the system, U, which is called the *internal energy*. If the internal energy of the system is U_1 in the initial state and U_2 in the final state, then

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* As the surface area increases so does the energy of the system, i.e., work is being done on the system.

** The essence of the law of conservation of energy is clearly expounded in Feynman, R., R. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. 1, London, 1963, on the basis of the proposition that "... *even the present-day physicists do not know what energy is*".

$$-W_{\text{ad}} = U_2 - U_1 = \Delta U \tag{2.14}$$

Thus, the work done upon the system in an adiabatic process is expended to increase its internal energy. In practice, however, the heat insulation of the system is always more or less imperfect. If we dismiss this idealization and consider closed systems, which are not heat-insulated, then Eq. (2.14) will not hold in a general case, i.e.,

$$W + \Delta U \neq 0 \tag{2.15}$$

This is an indication of the existence of certain external agencies which are different from work and capable of exerting an influence on the state of the closed system. On the basis of the foregoing let us define a certain quantity Q, i.e.,

$$Q = \Delta U + W \text{ (a closed system)} \tag{2.16}$$

and call it *heat*.* If $Q > 0$, the system absorbs heat and if $Q < 0$ the heat is given off to the surroundings. Relation (2.16) is the complete statement of the first law of thermodynamics:

The heat absorbed by the system is consumed to increase the internal energy of the system and to perform external work on its outside environment. The internal energy is an extensive property of the system.

Equation (2.16) can be rewritten in the form

$$-\Delta U = -Q + W \tag{2.17}$$

that is, *the decrease in internal energy of the system is consumed for the evolution of heat and for the performance of work.* This can be illustrated by an approximate example. Imagine an electric storage battery (for example, a starter storage battery for an automobile) in two states: state I—charged, internal energy U_1; state II—discharged, internal energy U_2. Then $U_1 > U_2$ and $U_2 - U_1 = \Delta U < 0$. Various ways can be suggested for discharging the storage battery, i.e., for the change of the system from state I to state II. These ways are shown in Fig. 2.2*a* and *b*. In the first case, the storage battery is short-circuited by a resistance coil. The energy of the electric discharge is completely converted to Joule heat, the amount of which is at a maximum:

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* The above reasonings, which lead to the formulation of the first law of thermodynamics, are due to Carathéodory and Born. In particular, the heat was determined by the method indicated by Max Born in 1921.

$$-\Delta U = Q_{\max} \tag{2.18}$$

No work is done in this case, i.e., $W = 0$.

Another way of discharging may, however, be proposed—the storage battery can be connected to an electric motor (Fig. 2.2*b*), which will raise a weight with the help of a pulley and tackle or do any other work. If the entire system works very slowly, the amount of heat evolved due to friction will be negligibly small, i.e., $Q = 0$ and

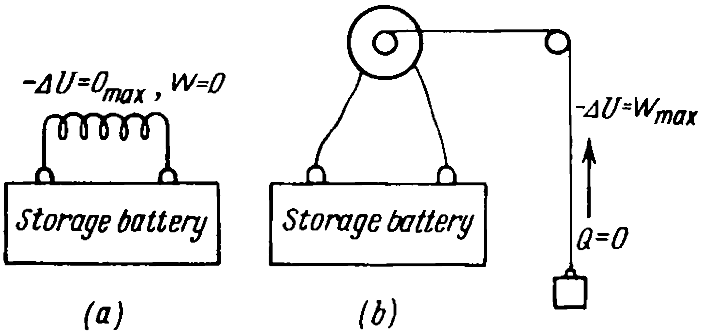

Fig. 2.2. Illustrating the first law of thermodynamics.

$$-\Delta U = W_{\max} \tag{2.19}$$

Hence, in the limit the amount of work on this path will prove to be a maximum. In the example given above it is important to understand the following: the difference $\Delta U = U_2 - U_1$ which expresses the change in internal energy of the system is independent of the path or method used to accomplish the process and depends only upon the initial and final states of the system with the values of internal energy U_1 and U_2. At the same time, the amounts of heat and work are in the most direct way associated with the path of the process—they are not the properties of the system, i.e., no inherent amounts of heat and work can be assigned to the system in a given state. Between the extreme cases defined by relations (2.18) and (2.19) there may be any number of intermediate cases when work is performed and heat is evolved simultaneously; all these cases must obey the relation $-\Delta U = -Q + W$. It is possible, however, to create conditions under which the heat evolved or absorbed by the system will be equal to the change in a property of the system and, hence, will be found to be independent of the path. This important case will be reated in detail in Sec. 2.5.

If the system undergoes only an infinitesimal change associated with the elementary amounts of heat and work, the first law should be written in the form

$$\delta Q = dU + \delta W \text{ (a closed system)} \qquad (2.20)$$

Here stress is made on the difference between the property of the system U, whose change is an exact differential, dU, and the infinitesimal amounts of heat and work δQ and δA which are not the properties of the system.

Phenomenological thermodynamics does not finalize the further content of the concept of the internal energy and, being incapable of defining the absolute value of internal energy for the system, manipulates only with the differences ($U_2 - U_1 = \Delta U$) of this quantity in two states.

From the viewpoint of the theory of the structure of a substance the internal energy may be regarded as the sum of all kinds of energy associated with the various motions and interactions that occur within the system. This includes the energy of molecules and the energy of intermolecular interaction. This could also include the "energy of mass" defined by the Einstein relation $E = mc^2$, where m is the mass and c is the velocity of light.

In chemistry one can most often restrict oneself to the consideration of systems subjected only to external forces. The system then performs only mechanical work $p\,dv$ and, instead of Eq. (2.20), we write:

$$\delta Q = dU + p\,dv \text{ (a closed system)} \qquad (2.21)$$

The first law of thermodynamics will be used mainly in this form.

2.4. Some Simple Applications of the First Law. The Work of Expansion and Compression of an Ideal Gas

A gas can be expanded in various ways. Let us first consider an *isothermal* process, i.e., the expansion or compression of a gas, a process that takes place at constant temperature. To do this, imagine a system consisting of a thermostat *2* which maintains a constant temperature in a cylinder *1* filled with a gas and closed with a piston, which moves without friction (Fig. 2.3). The cylinder is made of a material which conducts heat well, this providing an exchange of heat between the gas and the thermostat and, hence, a constant temperature. In order to expand the gas at constant temperature, it is necessary to constantly lower the external pressure. For this purpose, the piston can be loaded, for example, with fine sand which is removed, a grain at a time. The necessity for this procedure will be explained in detail in Sec. 2.9. As a result, the gas will be gradually expanded, the temperature will remain unchanged, and the pressure will decrease continuously in inverse proportion to the volume in accordance with Eq. (1.5):

$$p = \frac{nRT}{v}$$

Substituting this expression into the integral of (2.10), we obtain:

$$W_T = \int_{v_1}^{v_2} nRT \frac{dv}{v} = nRT \ln \frac{v_2}{v_1} \tag{2.22}$$

where the subscript (T) indicates the constancy of temperature, i.e., it may be taken outside the integral sign. Thus, the work of isothermal expansion of an ideal gas is proportional to the absolute temperature and is determined by the ratio of the final and initial volumes.

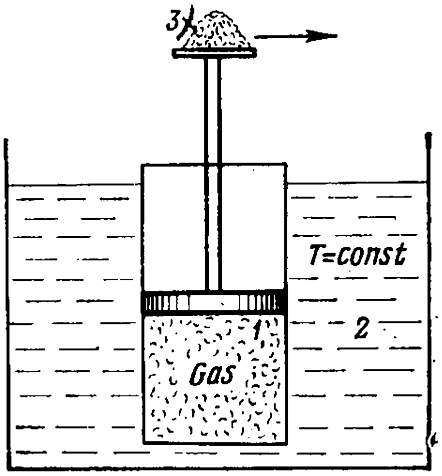

Fig. 2.3. Calculating the work of isothermal expansion:
1—cylinder with piston and gas; 2—thermostat; 3—weights equilibrating the gas pressure.

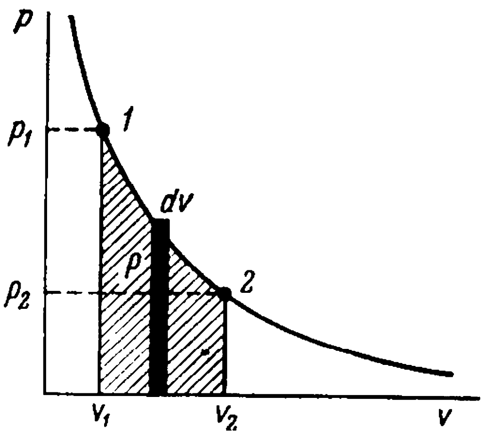

Fig. 2.4. Graphical representation o the work of isothermal expansion o an ideal gas.

In the coordinate system p-v the work of expansion is represented by an area (Fig. 2.4). In Fig. 2.4 the hyperbolic curve corresponds to Eq. (1.15). The element of work $\delta W = p\, dv$ will be expressed in the graph within infinitesimal values of second order by the area of the filled column, and the integral of (2.22), i.e., the work of finite isothermal expansion will be given by the area of the hatched figure dilineated by an isotherm portion, two ordinate segments and the abscissa.

As an example, we consider the computation of the work of isothermal expansion. Let us take one mole of gas and increase its volume by 10 times, i.e., $v_2/v_1 = 10$, at a temperature of 300°K. Using formula (2.22), we obtain:

$$W_T = 1.987 \times 300 \times 2.303 \log 10 = 1373 \text{ cal/mole}$$

The same work will be done with any values of the volumes, if their ratio is equal to 10, and at a temperature of 300°K. Of interest is the question of the source of the energy to be used to expand the ideal gas isothermally. An important property of the ideal gas is that its internal energy is independent of the volume or pressure; U depends only on temperature, i.e., $U = f(T)$ and

$$\left(\frac{\partial U}{\partial v}\right)_T = 0, \qquad \left(\frac{\partial U}{\partial p}\right)_T = 0 \tag{2.23}$$

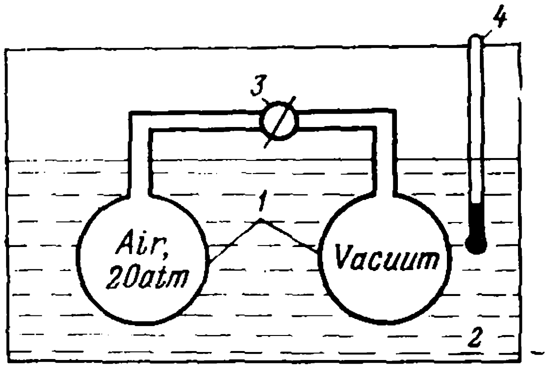

Fig. 2.5. Schematic representation of apparatus for the Joule-Gay-Lussac experiment:

1—copper containers; 2—water; 3—stopcock; 4—thermometer.

Relations (2.23) can be derived from the basic ideal gas equation and the second law of thermodynamics, as will be shown in Sec. 4.2. Originally, however, they were established on the basis of the experiments carried out by Gay Lussac and Joule. Joule's experiment, in essence, is carried out as follows: Two copper containers joined by a tube provided with a stopcock are immersed in a calorimeter bath (see Fig. 2.5). One of the containers holds a gas at a specified pressure (up to 20 atm) and temperature, and the other container has been evacuated. The experiment consists of opening the stopcock and allowing the gas to expand freely from one container into the other and then measuring the net temperature change attending the process after thermal equilibrium has been established. No change in the temperature of the water is observed, i.e., the containers neither absorb nor evolve heat to the surroundings, i.e., Q, the net quantity of heat that enters or leaves the system in the course of the experiment, is zero. Since no work is done during the expansion of the gas—the expansion into a vacuum, with no external force being overcome, it follows that W is also equal to zero. Hence, according to the first law, i.e., $Q = \Delta U + W$, the change in the internal energy $\Delta U = 0$. From this it is concluded that the internal energy of a gas is independent of the volume and pressure. True, more accurate experiments carried out later by Joule and Thomson showed that a certain change in the temperature (i.e., cooling or heating) does take place during the expansion of the gas into a vacuum. This phenomenon is known as the *Joule-Thomson effect*. As has been found, this effect is the smaller the lower the pressure of the gas and the higher the initial temperature, i.e., the more closely the behaviour of the gas is described by the equation $pV = nRT$. Therefore, the fact that the internal energy is independent of the volume or pressure was regarded as one of the properties of an ideal gas.

Thus, in the isothermal expansion of an ideal gas its internal energy in states (I) and (II) (see Fig. 2.4) is the same, i.e., $U_2 - U_1 = \Delta U = 0$. Hence, according to the first law

$$Q_T = W_T \tag{2.24}$$

and in order to do work under the conditions of constant temperature the gas must absorb an equivalent amount of heat from the thermostat. Now it is useful to rewrite formula (2.22) for the work of isothermal expansion of the ideal gas:

$$W_T = nRT \ln \frac{v_2}{v_1} = nRT \ln \frac{p_1}{p_2} = Q_T \tag{2.25}$$

where the inverse proportionality between pressure and volume is taken into account.

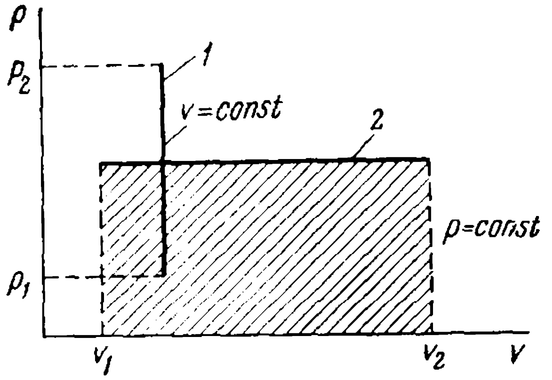

Fig. 2.6. An isochoric change in the gas pressure (*1*) and isobaric expansion (*2*).

Let us now consider a process involving an *isochoric* change in the pressure of the gas, i.e., a process that takes place at constant volume (v=const). Graphically, in the coordinate system p-v this process is expressed by a portion of a straight vertical line (see Fig. 2.6). To carry out such a process, it is necessary to heat the gas—the piston in the cylinder is fixed in a certain position and the cylinder is moved from one thermostat to another at a higher temperature. The work $p\,dv$ in the isochoric process is zero and the law (2.21) or (2.16) will give:

$$\delta Q_v = dU \quad \text{or} \quad Q_v = \Delta U \tag{2.26}$$

that is, the entire heat added is consumed to increase the internal energy of the gas.

We now introduce the concept of the *true heat capacity* C_v at constant volume. Generally, this quantity is defined by the relation

$$C_v \equiv \left(\frac{\delta Q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v \tag{2.27}$$

and represents the amount of heat per one degree increase in temperature. The true heat capacity as defined by relation (2.27) differs from the average heat capacity, which is the ratio of the finite values of Q and ΔT. The heat capacity is also referred to a certain amount of substance—the heat capacity per gram is called the specific heat and that for one mole of material is the molar heat capacity. In this book we shall use the molar true heat capacity expressed in calories:

$$\underline{C}_v \left[\frac{\text{calorie}}{\text{degree} \cdot \text{mole}} \right] \tag{2.28}$$

What has been said about C_v is of general importance, i.e., applies to any substances in all the states of aggregation.

If we return now to the ideal gas, expression (2.27) can be rewritten as follows, with account taken of the fact that the internal energy is independent of the volume:

$$C_v = \frac{dU}{dT} \tag{2.29}$$

or

$$dU = C_v dT \tag{2.30}$$

where dU is the increase in internal energy of one mole of the ideal gas upon heating by dT. For n moles of gas

$$dU = nC_v dT \tag{2.31}$$

In order to calculate the change in internal energy when the temperature has increased from T_1 to T_2 we integrate Eq. (2.31):

$$\Delta U = \int_{T_1}^{T_2} nC_v \, dT = n \int_{T_1}^{T_2} C_v \, dT \tag{2.32}$$

To evaluate the last integral it is necessary, generally speaking, to know the dependence of heat capacity on temperature, i.e., $C_v = f(T)$. In approximate calculations and when the change in temperature is not very large C_v may be considered to be a constant quantity. Taking the heat capacity outside the integral sign, we get:

$$\Delta U \approx nC_v (T_2 - T_1) \tag{2.33}$$

In using formula (2.33) one should not think that the constancy of heat capacity is a property of the ideal gas. This is not so; the heat capacity depends on temperature (see Sec. 2.7).

Let us now turn to the *isobaric expansion* of the gas. We take, as before, a cylinder with a gas and a piston loaded up to a pressure p. In this case too the piston must move freely in the cylinder, which is carried through a series of thermostats with a constantly increasing temperature. The gas is heated and expands from v_1 to v_2 at constant pressure. In the coordinate system p-v the process is expressed by a straight horizontal line and the work done by it is equal to

$$W_p = \int_{v_1}^{v_2} p \, dv = p (V_2 - V_1) = np (\underline{v}_2 - \underline{v}_1) \tag{2.34}$$

where V is the volume of an arbitrary amount of gas; v is the molar volume. In Fig. 2.6 the quantity W_p is represented by the area of the hatched rectangle. Using formula (2.34) for the ideal gas*, we replace the volumes with the aid of Eq. (1.5):

$$V_2 = n\frac{RT_2}{p} \quad \text{and} \quad V_1 = n\frac{RT_1}{p}$$

and obtain the relation

$$W_p = nR\,(T_2 - T_1)$$

which shows that the work of the isobaric (constant-pressure) process is proportional to the difference of the temperatures of the ideal gas. As for the change in its internal energy, it can be approximately calculated from formula (2.33), i.e.,

$$\Delta U = nC_v\,(T_2 - T_1) \tag{2.35}$$

Here the reader should not be embarrassed by the use of C_v at constant pressure, since the internal energy of the ideal gas is a funcion of temperature only; its change will be the same in the course of an isochoric (constant-volume), isobaric (constant-pressure) or any other process if the difference $T_2 - T_1$ is the same. Solving Eq. (2.34) for R, we can arrive at the following interpretation of the physical significance of the gas constant:

$$R = \frac{W_p}{n\,(T_2 - T_1)} \left[\frac{\text{work}}{\text{degree}\cdot\text{mole}}\right] \tag{2.36}$$

that is, the gas constant is equal to the work done by one mole of the ideal gas on heating by one degree at constant pressure.**

Let us now consider the true heat capacity at constant pressure. It is defined by the following relation:

$$C_p \equiv \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p \tag{2.37}$$

where the second part of the equality includes the expression of the first law of thermodynamics (2.21). It shows that the heat required to heat the body by one degree is consumed to increase the internal energy $\partial U/\partial T$ and to do work against the external constant pressure p overcome by the system during the expansion due to heating. The heat capacity at constant pressure will also be referred to one mole of substance, i.e.,

$$C_p\left[\frac{\text{calorie}}{\text{degree}\cdot\text{mole}}\right] \tag{2.38}$$

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* The formula for the work of an isobaric process in the form (2.34) applies to any system.

** See also Chapter 1, Sec. 1.2.

We shall now apply Eq. (2.37) to the ideal gas. First, the subscript emphasizing the constancy of the pressure can be dropped in the derivative of the internal energy and account can be taken of Eq. (2.29); then we have

$$C_p = \frac{dU}{dT} + p\left(\frac{\partial v}{\partial T}\right)_p = C_v + p\left(\frac{\partial v}{\partial T}\right)_p \tag{2.39}$$

Further, to find the derivative of the volume with respect to temperature we make use of the equation of state of the ideal gas and obtain $C_p = C_v + R$ or

$$C_p - C_v = R \tag{2.40}$$

Equation (2.40) is consistent with Eq. (2.36), in which the gas constant equals the work done by one mole of gas on heating by one degree at constant pressure. It is this work which is done due to the absorption of an additional amount of heat equal to R.

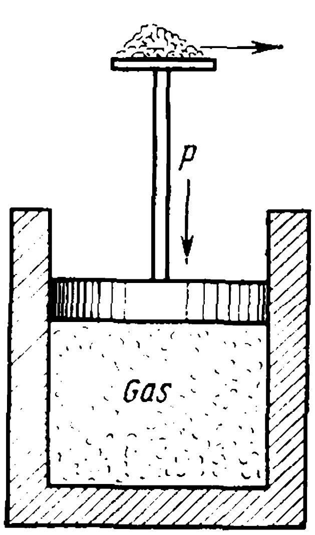

Fig. 2.7. Cylinder for carrying out the adiabatic expansion of a gas.

We shall now turn to the *adiabatic* process of expansion-compression of the gas. An adiabatic process is one in which no heat enters or leaves the system, i.e., Q is equal to zero or

$$\delta Q = 0 \tag{2.41}$$

Suppose we have a cylinder and a piston made of a material which does not conduct heat (Fig. 2.7). Just as in the case of an isothermal expansion, the piston is considered to be loaded with fine sand which balances the gas pressure p. Removing one grain at a time, we gradually reduce the external pressure. The gas begins to expand, thereby doing work without absorbing heat. According to the first law of thermodynamics in the form (2.20), we obtain $dU + \delta W = 0$ or

$$\delta W = -dU = p\,dv \tag{2.42}$$

that is, the work will be done due to the loss of the internal energy of the gas, which must cool off.

Let us derive the relationship between volume and pressure in an adiabatic process; since $dU = C_v dT$, from Eq. (2.42) we have

$$C_v\,dT + p\,dv = 0 \tag{2.43}$$

We replace p from the ideal gas equation and divide by T:

$$C_v \frac{dT}{T} + R \frac{dv}{v} = 0 \tag{2.44}$$

In this equation the variables are separated and it can be integrated approximately, assuming that C_v is independent of temperature:

$$C_v \ln T + R \ln v = \text{const} \tag{2.45}$$

where const is the integration constant. Or, combining the logarithms,

$$\ln T^{C_v} v^R = \text{const} \tag{2.46}$$

If the logarithm is constant, the logarithmic function is also constant, i.e.,

$$T^{C_v} v^R = \text{const} \tag{2.47}$$

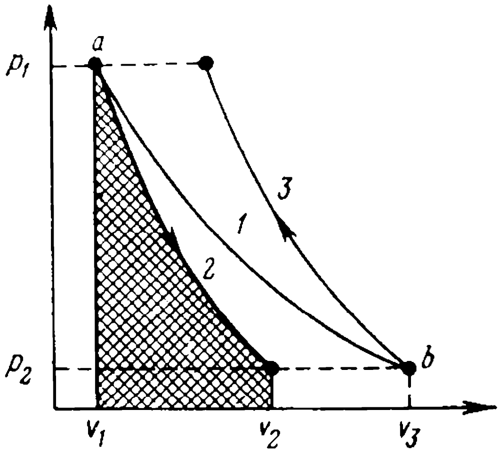

Fig. 2.8. Comparison of the isothermal and adiabatic processes of expansion and compression of an ideal gas: 1—isotherm; 2—adiabatic expansion; 3—adiabatic compression.

This is precisely one of the forms of the equations of the adiabatic curve relating the volume to the temperature of the gas. Replacing the temperature in the ideal gas equation, we write:

$$p^{C_v} v^{C_v} v^R = \text{const}\, R^{C_v} \tag{2.48}$$

Or, finally, combining the exponents of the volume, extracting the root of the exponent C_v and also incorporating R into the common constant, we get:

$$pv^{\frac{C_p}{C_v}} = pv^k = \text{const} \tag{2.49}$$

where k is the ratio of the heat capacity at constant pressure to that at constant volume; $k > 1$. In this case, with an adiabatic change in the volume the pressure changes more rapidly than it does at constant temperature. To the conditions of the adiabatic curve there approximately corresponds the rapid occurrence of the process of compression or expansion when the relatively slow heat exchange affects little, within the time period of interest, the change of the internal energy of the gas and its temperature (Fig. 2.8). If the gas is expanded adiabatically, starting from point a, then the curve 2 will be steeper than the isotherm 1 and the same pressure will be attained at a smaller volume since the adiabatic expansion is accompanied by cooling. On the contrary, if an adiabatic compression is carried out by starting from the state at point b, then the equal pressure p_1 will be reached at a larger volume as compared with the isotherm; the cause is the heating of the gas.

Let us derive the formula for calculating the work of an adiabatic process. We substitute the pressure from Eq. (2.49) into the work integral, (2.42), and obtain:

$$W_Q = \int_{v_1}^{v_2} \frac{\text{const}}{v^k}\, dv = \frac{\text{const}\, v_2^{1-k} - \text{const}\, v_1^{1-k}}{1-k} \tag{2.50}$$

But in accordance with Eq. (2.49) const $= p_1 v_1^k = p_2 v_2^k$; therefore, rearranging Eq. (2.50), we get the following formula:

$$W_Q = \frac{p_1 v_1 - p_2 v_2}{k-1} \tag{2.51}$$

which expresses the work of the adiabatic process in terms of the initial and final values of pressure and volume. The work will be represented by the area of the hatched figure (Fig. 2.8). If the ideal gas equation $pV = nRT$ is used, Eq. (2.51) can be given in the following form:

$$W_Q = nC_v (T_1 - T_2) \tag{2.52}$$

It thus follows that the adiabatic work is proportional to the temperature difference. Further, taking account of the dependence of the internal energy of the ideal gas on temperature, we make use of the approximate formula (2.33) to obtain the relation

$$W_Q = -\Delta U = U_1 - U_2 \tag{2.53}$$

from which it is seen that in the adiabatic process the work is done due to the loss in the internal energy. The same relation follows immediately from Eq. (2.42).

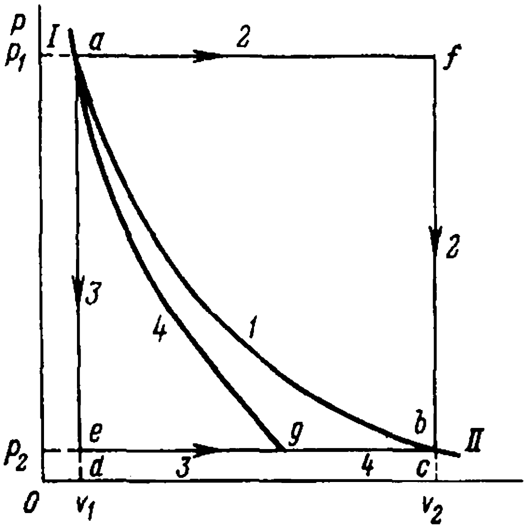

Fig. 2.9. Comparison of various paths for the transition of a gas from state I to state II which lie on the same isotherm:

The change in energy for all the paths is the same since $\Delta U = 0$ and the works and heats for transition paths (1), (2), (3), and (4) $W_i = Q_i$ are quite different.

In order to elucidate the difference between heat and work, on the one hand, and the internal energy, on the other, let us compare various paths by which the ideal gas is changed from one state to another. We choose two states on the isotherm 1 (Fig. 2.9), in which case we have

$$p_1 v_1 = p_2 v_2$$

With the isothermal path the work calculated from Eq. (2.25) is equal to the area of the figure *abcd*. However, starting from state I, we can first expand the gas at constant pressure to volume v_2 (point *f*) and then cool it at constant volume (the isochoric line *fc*). In this case the work equals the area of a considerably larger figure *afcd* (path *2*). Or, starting from state I, we first cool the gas, "descend" the isochoric line *ae* and then expand it at constant pressure p_2 along the isobaric line *eb*. The work is equal to the area of a small rectangle *ebcd* (path *3*). Finally, suppose the adiabatic expansion occurs along the curve *ag* and the completing constant-pressure process at pressure p_2 proceeds from point *g* to point *b*. In this latter case, the work will equal the area of a complex figure *agbcd* (path *4*). Thus, the four different paths (any number of paths could have been suggested) joining two identical states are associated with different amounts of work being done. As regards the change in internal energy, it is the same in all the cases, namely it is equal to zero ($\Delta U = 0$) since states I and II have, by the condition, the same temperature. Hence, according to the first law

$$W_i = Q_i \tag{2.54}$$

that is, the amounts of heat absorbed along the paths *1*, *2*, *3*, and *4* (or any other path joining states with the same temperature) are equal to the corresponding amounts of work. This example shows the difference between the internal energy, i.e., an inherent property of the system, and, on the other hand, the heat and work, the amounts of which are associated with the character of the change of the system, i.e., the path by which the process is accomplished. The change in a property of the system, i.e., the internal energy in this particular case, is independent of the path and is determined only by the initial and final states of the system.

2.5. Application of the First Law to Multicomponent Closed Systems. Thermal Coefficients. A Chemical Variable

Let us consider a multicomponent homogeneous system which contains $n_1, n_2, \ldots, n_c$ moles of substances. We choose the volume and temperature as the independent variables. The internal energy of the system can then be expressed as follows:

$$U = U(T, v, n_1, n_2, \ldots, n_c) \tag{2.55}$$

Since the system is closed, by definition, its total mass remains constant and the changes in the number of moles n_i are possible only due to chemical reactions. For the sake of simplicity, we assume that only a single reaction proceeds in the system:

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightarrow \nu_1' B_1' + \nu_2' B_2' + \ldots$$

Suppose that the reaction has proceeded from left to right, so that the numbers of moles of the reactants and products have been changed —the number of moles of substance B_1 by dn_1, that of substance B_2 by dn_2, and those of substances B_1' and B_2' by dn_1' and dn_2', etc. Then, if the system originally contained $n_1^0, n_2^0, \ldots n_1'^0, n_2'^0, \ldots$ moles, the function (2.55) may be given in a form analogous to (1.78):

$$U = U(T, v, \xi, n_1^0, n_2^0, \ldots, n_1'^0, n_2'^0, \ldots) \tag{2.56}$$

where ξ is a chemical variable (1.76). If we agree to restrict ourselves to the given system of the initial composition indicated, then Eq. (2.56) may be written in an abbreviated form:

$$U = U(T, v, \xi) \tag{2.57}$$

We shall now write the exact differential of the internal energy:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{v,\xi} dT + \left(\frac{\partial U}{\partial v}\right)_{T,\xi} dv + \left(\frac{\partial U}{\partial \xi}\right)_{T,v} d\xi \tag{2.58}$$

Substituting it into the expression for the first law (2.21)

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_{v,\xi} dT + \left[p + \left(\frac{\partial U}{\partial v}\right)_{T,\xi}\right] dv + \left(\frac{\partial U}{\partial \xi}\right)_{T,v} d\xi \tag{2.59}$$

and introducing then abbreviated notations for the coefficients before the differentials of the independent variables, we define the so-called *thermal coefficients:*

$$\left(\frac{\partial U}{\partial T}\right)_{v,\xi} \equiv C_{v,\xi}; \quad p + \left(\frac{\partial U}{\partial v}\right)_{T,\xi} \equiv l_{T,\xi}; \quad \left(\frac{\partial U}{\partial \xi}\right)_{T,v} \equiv U_{T,v} \tag{2.60}$$

Thus, the first law of thermodynamics assumes the following form:

$$\delta Q = C_{v,\xi}\, dT + l_{T,\xi}\, dv + U_{T,v}\, d\xi \tag{2.61}$$

Let us now examine the physical significance of each of the thermal coefficients. If the volume of the system remains constant (i.e., v = const and $dv = 0$) and no chemical reaction takes place ($d\xi = 0$), then from Eq. (2.61) we obtain:

$$\delta Q_{v,\xi} = C_{v,\xi}\, dT = \left(\frac{\partial U}{\partial T}\right)_{v,\xi} dT$$

where $\delta Q_{v,\xi}$ is the heat absorbed by the system when it is heated by dT under the above-indicated conditions of constant v and ξ. Hence, $C_{v,\xi}$ is the heat capacity of a multicomponent system at constant volume and composition. In a special case, if we have a one-component and homogeneous system, its total heat capacity will be expressed in terms of the molar heat capacities of a pure substance, $\underline{C}_v$ (2.28):

$$C_{v,\xi} = \tilde{C}_v = n\underline{C}_v \tag{2.62}$$

In a general case, however, this extensive property of the multicomponent system must be calculated in terms of the partial molar heat capacities of the components, i.e., in accordance with a relation of type (1.70):

$$C_{v,\xi}=\sum_i n_i\overline{C}_{vi} \tag{2.63}$$

where $\overline{C}_{vi}$ is an intensive quantity defined by the derivative

$$\overline{C}_{vi}=\left(\frac{\partial C_{v,\xi}}{\partial n_i}\right)_{T,\,p,\,n_j\neq n_i} \tag{2.64}$$

It may be noted that though $\overline{C}_{vi}$ differs, generally speaking, from the molar heat capacity $\underline{C}_v$ and depends on the composition of the mixture, there is no such difference for ideal gases, and for real gases it may prove to be insignificant if the pressure is not too high. In any case, this difference is neglected and the heat capacities are calculated from the molar heat capacities of the components.

Let us now consider possible isothermal changes ($dT = 0$) in the system at constant composition ($d\xi = 0$). In this case, from Eq. (2.61) we have

$$\delta Q_{T,\xi}=l_{T,\xi}\,dv=\left[p+\left(\frac{\partial U}{\partial v}\right)_{T,\xi}\right]dv \tag{2.65}$$

We see that $l_{T,\xi}\,dv$ is the heat of an isothermal change in volume of the system at constant composition, this heat being spent to produce a change in the internal energy (to overcome the forces of intermolecular interaction) and for performing the mechanical work $p\,dv$. Since for an ideal gas $(\partial U/\partial v)_T = 0$ in accordance with Eq. (2.23), then in this case we have

$$l_{T,\xi}=p$$

Let us turn to a case which is of prime importance to the chemist. The temperature and volume of the system remain constant, i.e., $dT = 0$ and $dv = 0$, and the chemical variable ξ undergoes a change —a chemical reaction is taking place (see page 56). The heat of the process will then be expressed as follows in accordance with Eqs. (2.61) and (2.59):

$$\delta Q_{T,v}=U_{T,v}\,d\xi=\left(\frac{\partial U}{\partial \xi}\right)_{T,v}d\xi$$

and the thermal coefficient $U_{T,v}$ will define the differential heat effect of the reaction at constant temperature and volume. In other words, $U_{T,v}$ is the heat that enters or leaves the system at constant T and v per unit reaction but with an infinitesimal change in the composition of the system. The quantity $U_{T,v}$ may also be called the *true heat effect* of reaction at constant temperature and volume in the same sense as the true reaction velocity (the velocity at a given point) or true heat capacity is defined. Strictly speaking, the differential heat effect should not be confused with the usually determined average heat effect $\Delta U_{T,v} = Q_{T,v}$ (see page 61 for more details).

Let us now consider another combination of the independent variables, namely, T, p and ξ and express the dependence of the internal energy on these variables:

$$U = U(T, p, \xi) \tag{2.66}$$

We write the exact differential of U:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial U}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial U}{\partial \xi}\right)_{T,p} d\xi \tag{2.67}$$

Moreover, the volume must also be considered to be a function of T, p and ξ:

$$v = v(T, p, \xi) \tag{2.68}$$

and

$$dv = \left(\frac{\partial v}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial v}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial v}{\partial \xi}\right)_{T,p} d\xi$$

Now both differentials are substituted into the expression for the first law:

$$\delta Q = \left[\left(\frac{\partial U}{\partial T}\right)_{p,\xi} + p\left(\frac{\partial v}{\partial T}\right)_{p,\xi}\right] dT + \\ + \left[\left(\frac{\partial U}{\partial p}\right)_{T,\xi} + p\left(\frac{\partial v}{\partial p}\right)_{T,\xi}\right] dp + \left[\left(\frac{\partial U}{\partial \xi}\right)_{T,p} + p\left(\frac{\partial v}{\partial \xi}\right)_{T,p}\right] d\xi \tag{2.69}$$

We now introduce the following notations:

$$C_{p,\xi} \equiv \left(\frac{\partial U}{\partial T}\right)_{p,\xi} + p\left(\frac{\partial v}{dT}\right)_{p,\xi} \tag{2.70}$$

$$h_{T,\xi} \equiv \left(\frac{\partial U}{\partial p}\right)_{T,\xi} + p\left(\frac{\partial v}{\partial p}\right)_{T,\xi} \tag{2.71}$$

and

$$h_{T,p} \equiv \left(\frac{\partial U}{\partial \xi}\right)_{T,p} + p\left(\frac{\partial v}{\partial \xi}\right)_{T,p} \tag{2.72}$$

and rewrite the first law with the aid of new thermal coefficients:

$$\delta Q = C_{p,\xi}\, dT + h_{T,\xi}\, dp + h_{T,p}\, d\xi \tag{2.73}$$

Examining this formula, we arrive at the following conclusions. The coefficient $C_{p,\xi}$ is the heat capacity of the entire multicomponent system at constant pressure and composition. Like $C_{v,\xi}$, it is connected with the partial molar heat capacities of the components of the system by Euler's equation:

$$C_{p,\xi}=\sum_{i=1}^{c} n_i\bar{C}_{pi} \tag{2.74}$$

where

$$\bar{C}_{pi}=\left(\frac{\partial C_{p,\xi}}{\partial n_i}\right)_{T,\,p,\,n_j\neq n_i} \tag{2.75}$$

For a pure substance in a single phase (a homogeneous one-component system) the partial molar heat capacity is simply equal to the molar heat capacity, and the heat capacity of the system is given by

$$C_{p,\xi}=\bar{C}_p=n\underline{C}_p$$

Thus, the heat capacity of the mixture, $C_{p,\xi}$, must, strictly speaking, be determined from the partial molar heat capacities $\bar{C}_{pi}$ (2.75). In most actual cases, however, the values of $\bar{C}_{pi}$ are unknown and therefore the partial molar heat capacities are often replaced by the molar heat capacities of pure substances. This approximate calculation furnishes quite acceptable results for gas mixtures, whose behaviour does not differ greatly from that of ideal gases. In the latter case, applying the ideal gas law and relation (2.70), we find: $C_{p,\xi} = C_{v,\xi} + nR$, where $n = \Sigma n_i$ is the total number of moles of a mixture of ideal gas.

The coefficient $h_{T,\xi}$ represents the heat of an isothermal change in the pressure of the system at constant composition. Like other thermal coefficients of this series, the given heat is defined by two terms—the change in internal energy $(\partial U/\partial p)_{T,\xi}$ and the mechanical work $p\ (\partial v/\partial p)_{T,\xi}$, which is related to the change in the volume, depending on the pressure. Applying the definition (2.71) to ideal gases, we become convinced that

$$h_{T,\xi}=-V \tag{2.76}$$

That is, the coefficient $h_{T,\xi}$ is equal to the total volume of the system with a minus sign. In this connection, it is said that $h_{T,\xi}$ is an essentially negative quantity. The coefficient

$$h_{T,p}\equiv\left(\frac{\partial U}{\partial\xi}\right)_{T,p}+p\left(\frac{\partial v}{\partial\xi}\right)_{T,p}=\frac{\delta Q_{T,p}}{\partial\xi} \tag{2.77}$$

expresses the differential (true) heat effect of a chemical reaction at constant pressure and temperature. In expression (2.77) again two terms can be distinguished: the change in internal energy attending the reaction, i.e., $(\partial U/\partial\xi)_{T,p}$, and the mechanical work done during the change in the volume due to the reaction, i.e., $p\ (\partial v/\partial\xi)_{T,p}$.

The thermal coefficients $C_{p,\xi}$, $h_{T,\xi}$ and $h_{T,p}$ can be written down in a more compact form if we introduce a new thermodynamic function—the *enthalpy* (or *heat content*) defined by

$$H \equiv U + pv \tag{2.78}$$

This definition of enthalpy applies to systems which are subjected to the action of external pressure only. The enthalpy is an extensive property and has the dimensions of energy. The enthalpy is sometimes called the total energy of the system equal to the sum of the internal energy U and the "volume energy" pv. Using the enthalpy, we arrive at the following expressions for the thermal coefficients:

$$C_{p,\xi} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \tag{2.79}$$

$$h_{T,\xi} = \left(\frac{\partial H}{\partial p}\right)_{T,\xi} - v \tag{2.80}$$

$$h_{T,p} = \left(\frac{\partial H}{\partial \xi}\right)_{T,v} \tag{2.81}$$

In this section we have defined quantities which are of fundamental importance to chemistry—the differential heat effects of the reaction, $U_{T,v}$ and $h_{T,p}$. Strictly speaking, thermochemistry usually deals not with these differential characteristics but with the averaged quantities, $Q_{T,v} = \Delta U_{T,v}$ and $Q_{T,p} = \Delta H_{T,p}$. In order to establish the relationship and the difference between the first and second quantities we are to define the partial molar enthalpy of a component of a system—a participant in the reaction:

$$\bar{h}_i \equiv \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_j \neq n_i} \tag{2.82}$$

Further, suppose that we have a multicomponent system containing all the substances that take part in the reaction:

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightarrow \nu_1' B_1' + \nu_2' B_2' + \ldots \tag{2.83}$$

In the given state of the system the partial molar enthalpy $\bar{h}_i$ can be assigned to each of the participants. Then, $\bar{h}_i dn_i$ will represent the change in enthalpy of the system associated with the change in the number of moles of a given component by dn_i. The total change in the enthalpy during the change in the amounts of all the reactants and products is expressed, in accordance with the stoichiometry of the reaction equation, as follows:

$$dH_{T,p} = \bar{h}_1 dn_1 + \bar{h}_2 dn_2 + \ldots + \bar{h}_1' dn_1' + \bar{h}_2' dn_2' + \ldots \tag{2.84}$$

But according to the definition of the chemical variable $dn_i = \pm \nu_i d\xi$; so

$$dH_{T,p} = (\nu_1' \bar{h}_1' + \nu_2' \bar{h}_2' + \ldots - \nu_1 \bar{h}_1 - \nu_2 \bar{h}_2 - \ldots)\, d\xi \tag{2.85}$$

or

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,\,p}=\nu_1'\bar{h}_1'+\nu_2'\bar{h}_2'+\ldots-\nu_1\bar{h}_1-\nu_2\bar{h}_2-\ldots=\sum \nu_i\bar{h}_i=h_{T,\,p} \tag{2.86}$$

Relation (2.86) defines the differential heat of reaction in terms of the partial molar enthalpies of the participants.

In practice, however, as has already been said, not the differential (true) heat effects are determined and used in thermochemistry but the integral quantities corresponding to a finite change in the chemical variable by unity ($\Delta\xi = 1$), i.e., to one equivalent of reaction. How are the differential and integral heat effects interrelated? Recall that the enthalpy, like all other extensive properties of the system, is a homogeneous function of the number of moles of the components of the system. Therefore, in dealing with a mixture of all the reactants, we can make use of Euler's theorem on homogeneous functions and write down [see Eq. (1.70)]:

$$\nu_1'h_1'+\nu_2'h_2'+\ldots=H_2 \tag{2.87}$$

and

$$\nu_1h_1+\nu_2h_2+\ \ldots=H_1 \tag{2.88}$$

Here H_1 will be equal to the enthalpies of the reactants in the mixture taken in amounts ν_1, ν_2 ... moles, and H_2 will be equal to the enthalpies of the products taken in amounts ν_1', ν_2' ... moles. Let us now suppose that the reaction has proceeded one equivalent in the system ($\Delta\xi = 1$), the values of partial molar enthalpies remaining unchanged. This can take place, for example, if the numbers of moles of the components, n_1, n_2, ..., n_1', n_2', ... are very large as compared with the numbers of moles reacted, ν_1, ν_2, ..., ν_1', ν_2', ... Then, $-H_1 = -(\nu_1h_1 + \nu_2h_2 + \ldots)$ represents the decrease in enthalpy of the system due to the loss of the reactants corresponding to $\Delta\xi = 1$, and H_2 represents the increase in enthalpy of the system due to the appearance in it of ν_1', ν_2' ... moles of the products. In this case, Eq. (2.86) can be rewritten thus

$$\frac{\delta Q_{T,\,p}}{\partial\xi}=\left(\frac{\partial H}{\partial \xi}\right)_{T,\,p}=h_{T,\,p}=H_2-H_1=\Delta H_{T,\,p}=Q_{T,\,p} \tag{2.89}$$

where $\Delta H_{T,p} = Q_{T,p}$ is the integral heat effect of reaction at constant pressure and temperature.

What has been said above may well apply to constant temperature and volume:

$$\frac{\delta Q_{T,\,v}}{\partial\xi}=\left(\frac{\partial U}{\partial \xi}\right)_{T,\,v}=U_{T,\,v}=U_2-U_1=\Delta U_{T,\,v}=Q_{T,\,v} \tag{2.90}$$

Thus, the heat effects of chemical reactions at constant temperature and volume or at constant temperature and pressure can be represented in the form of the difference of the properties of the system in two states, i.e., the difference in enthalpies or internal energies. This leads to an important thermochemical relationship—Hess's law which will be considered in Sec. 2.6.

In view of Eqs. (2.89) and (2.90) it must be clear that, strictly speaking, the differential and integral heat effects are equal in cases where the partial molar enthalpies (or internal energies) do not change during the course of the reaction. As has already been said, it is possible if the composition of the reacting mixture remains constant—the reaction has proceeded one equivalent in a large amount of the mixture. This also applies to a reaction taking place in a mixture of ideal gases since the internal energy and enthalpy of an ideal gas do not depend on the pressure (or concentration) and are functions of temperature only. In general, however, the relations between the differential and integral effects are rather complicated. Therefore, in practice the quantities that are determined are the so-called *standard heats* ΔH°_T or ΔU°_T, i.e., the heat effects of a reaction that takes place as though it occurred between pure substances (for example, each reactant is in a separate vessel). Each of the substances is in a certain state adopted as the standard state*. Since the partial molar quantities (for example, the enthalpies) of pure substances are simply equal to the molar values, then in the sum (2.86) there appear, instead of the partial molar enthalpies, the molar enthalpies of the substances in their standard states and we can write:

$$h^\circ_{T,\,p} = \sum \nu_i \underline{H}^\circ_i = \nu'_1 \underline{H}^{\circ\prime}_1 + \nu'_2 \underline{H}^{\circ\prime}_2 + \ldots - \nu_1 \underline{H}^\circ{}_1 - \nu_2 \underline{H}^\circ_2 - \ldots = \Delta H^\circ_{T,\,p}$$

where $\underline{H}^\circ_i$ are the molar enthalpies of the participants in their standard states. Thus, the standard differential and integral heats are equal to each other.

2.6. Basic Laws of Thermochemistry. Hess's Law **

The basic concept in thermochemistry is the concept of the heat effect introduced in Sec. 2.5. It will not suffice to say that the heat effect is the *heat evolved or absorbed in a chemical reaction*. This is correct provided that the following conditions are fulfilled: (1) volume or pressure is constant (v = const or p = const); (2) no work is being done, except for the work of expansion possible at p = const; (3) the temperature of the products is equal to that of the reactants. With these conditions the heat of reaction becomes a quantity which is most definite and depends only on the nature of the chemical reaction involved. Take, as an example, condition *3*. The amount of heat evolved will be lower if the products are obtained at a higher temperature than the temperature of the reactants. An extra amount of heat can be obtained if the products are cooled down to the initial temperature.

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* The standard states will be discussed in more detail in Sec. 2.6.

** In this and the subsequent sections we have adopted an elementary system of presentation; this problem will be treated more fully in Sec. 2.5.

Let us consider the second condition. In Sec. 2.3 where the first law was illustrated by the example of an electric storage battery, the operation of which is based on the known chemical conversions of lead or other substances, it was shown that, depending on the work done the amount of heat evolved undergoes a change from a certain maximum value $Q_{\max}$ to zero [relations (2.18) and (2.19)]. Thus, with the first condition being observed, i.e., at constant volume, no work whatsoever is done, and at constant pressure the only work done is the work of expansion $p(v_2 - v_1)$, where v_2 is the volume of the reaction products and v_1 is the volume of the reactants at the same temperature.

In accordance with the first condition a distinction is made in thermochemistry between the heat of chemical reactions at constant volume Q_v, and that at constant pressure, Q_p. Let us first examine a reaction at constant volume. Suppose the system is in two states. The state I is a mixture of one mole of nitrogen and three moles of hydrogen, which occupy the volume v at temperature T and pressure p and which have an internal energy U_1. The state II is two moles of ammonia at the same volumes and temperature but at a different pressure and with a different internal energy, U_2. Having applied the first law (2.21) to the process in question, we find that since, by convention, the work $W = 0$, the amount of heat evolved in the reaction, Q_v, is equal to the change in internal energy of the system, i.e.,

$$Q_v = U_2 - U_1 = \Delta U \tag{2.91}$$

where, as has already been said, U_2 is the internal energy of the reaction products and U_1 is the internal energy of the reactants. Relation (2.91) shows that, although the heat is not a property of the system, the heat of the chemical reaction at constant volume equals the change in internal energy of the system, i.e., its property, and is independent of the path of the process. By the term path is meant the number of various intermediate states (or steps) upon transition of the system from the initial to the final state. Thus, for example, in one case the formation of ammonia proceeds supposedly through hydrazine as an intermediate product, and in the other, the hydrogen molecule dissociates, for some reason, into its free atoms, or some excited state of the nitrogen molecule may first appear, and so on. Regardless of the difference between these paths, the heat of the reaction $N_2 + 3H_2 = 2NH_3$, which proceeds at a given constant volume and constant temperature, will be the same. This generalization is known as *Hess's law of constant heat summation.*

Let us now turn to a constant-pressure reaction (p = const). In a general case, the process is associated with the change in volume and with the work of expansion (or compression) $W_p = p(v_2 - v_1)$. In the synthesis of ammonia, the volume of the reaction products, v_2, is smaller than the volume of the reactants, v_1, i.e., the volume is reduced during the course of the reaction and the external pressure does work on the system. We use the first law in the form (2.21) with account taken of Eq. (2.34) for reactions at constant pressure:

$$Q_p = U_2 - U_1 + p(v_2 - v_1) = \Delta U + p\Delta v \qquad (2.92)$$

We rearrange expression (2.92)

$$Q_p = (U_2 + pv_2) - (U_1 + pv_1) \qquad (2.93)$$

and represent the property of the system $H \equiv U + pv$ as the difference between the values. The latter relation defines [as is known, (2.78)] the enthalpy of the system. Since definite values of U, p and v can be assigned to any state, the enthalpy too will have a definite value in any state.

Thus, the heat of reaction at constant pressure can also be defined as the change in a property of the system, i.e.,

$$Q_p = H_2 - H_1 = \Delta H \qquad (2.94)$$

where H_1 is the enthalpy of the reactants and H_2 is the enthalpy of the products. In other words, Q_p, like Q_v, is independent of the reaction path.

The enthalpy may also be regarded as a certain "total energy", i.e., as the sum of the internal energy U and the "volume energy" pv. The physical significance of H is, however, most distinctly seen in relation (2.94): the difference in enthalpy between two states of the system equals the heat of an isobaric process.

Relations (2.91) and (2.94) allow us to formulate the basic law of thermochemistry—Hess's law: *the heat of a chemical reaction at constant volume or constant pressure is independent of the path taken by the reaction, i.e., the number of steps which may intervene between the reactants and products, and depends only on the nature and conditions of the initial reactants and final products.* This law was enunciated in 1836 by Hess, Professor of the Mining Institute in Petersburg, on the basis of a comparison of experimental data.

Before considering examples illustrating the use of Hess's law, we should agree upon the notations to be used. Thermochemical tables usually give heats at constant pressure denoted by the symbol ΔH in accordance with Eq. (2.94). This symbol is used not only for chemical reactions but also for the heats of other constant-pressure processes—the heats of phase transitions. Thus, the heat of vaporization is designated as

$$\Delta H_{\text{vapn}}\left[\frac{\text{calorie}}{\text{mole}}\right] \tag{2.95}$$

and the heat of melting (fusion) as

$$\Delta H_{\text{m}}\left[\frac{\text{calorie}}{\text{mole}}\right] \tag{2.96}$$

and so on. The symbols l and λ, which were formerly used to denote these heats, are out of use now. The heat of reaction at constant pressure is denoted by ΔH_T°, where the subscript signifies the temperature corresponding to a given value of the heat of reaction; the superscript signifies that the reactants are in standard states (for more detail, see page 67). In view of what has been said, the heat at constant pressure, $Q_p = \Delta H$, is called the enthalpy change in a reaction or most often simply the *enthalpy of reaction.*

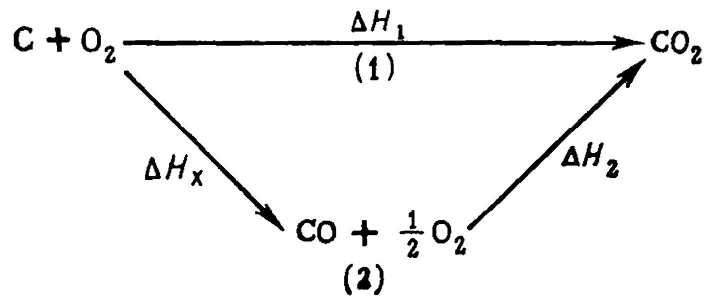

Fig. 2.10. Illustrating the use of Hess's law.

Hess's law of heat summation allows one to determine the heats of reactions which are either impossible to measure directly or have not been measured for some reason. For example, using Hess's law, one can calculate the heat of the reaction of formation of carbon monoxide from carbon and oxygen:

$$C+\frac{1}{2}O_2=CO \quad \Delta H_x=? \tag{2.97}$$

which cannot be measured directly. This reaction cannot be carried out in pure form since a certain amount of carbon dioxide is always formed. One can, however, measure the heats of the following reactions:

$$C+O_2=CO_2 \quad \Delta H_1=-94.0 \text{ kcal/mole} \tag{2.98}$$

$$CO+\frac{1}{2}O_2=CO_2 \quad \Delta H_2=-67.6 \text{ kcal/mole} \tag{2.99}$$

The minus sign for the heat means the decrease in enthalpy, i.e., $H_2 < H_1$, and heat is evolved, which corresponds to an exothermic reaction.

Using Eqs. (2.98), (2.99) and (2.97), we can draw a scheme for two possible paths of the formation of carbon dioxide (Fig. 2.10). The first path is the direct formation. The second path involves the formation of an intermediate product—carbon monoxide. According to Hess's law, $\Delta H_1 = \Delta H_x + \Delta H_2$ or

$$\Delta H_x = \Delta H_1 - \Delta H_2 = -94.0 + 67.6 = -26.4 \text{ kcal/mole} \tag{2.100}$$

As a further example, let us determine the heat of conversion of graphite into diamond:

$$\text{C (graphite)} \rightarrow \text{C (diamond)} \tag{2.101}$$

which cannot be measured directly. It is possible, however, to burn graphite and diamond separately and to determine the heats of the reactions:

$$\begin{array}{c} \text{C (graphite)} + O_2 = CO_2 + \Delta H_1 \\ \text{C (diamond)} + O_2 = CO_2 + \Delta H_2 \\ \hline \text{C (graphite)} - \text{C (diamond)} = \Delta H_1 - \Delta H_2 \end{array} \tag{2.102}$$

Hess's law permits one to manipulate with thermochemical equations in the same way as it is done with algebraic equations, i.e., to add or subtract them provided that the heat effects refer to the same conditions. Subtracting the second equation in (2.102) from the first, we obtain the third line, and when C (diamond) is transposed to the right side of the equation, we get Eq. (2.101) with $\Delta H_x = \Delta H_1 - \Delta H_2 = 453.2$ cal/g-atom. Thus, the conversion (2.101) is accompanied by the absorption of a small amount of heat.

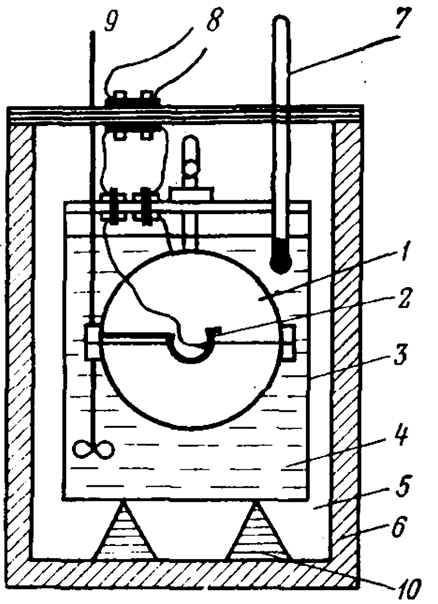

Fig. 2.11. A schematic of a calorimeter bomb and a water calorimeter for the determination of heats of combustion:
1—calorimeter bomb; 2—sample cup; 3—calorimeter jacket; 4—water; 5—air; 6—insulating well; 7—thermometer; 8—ignition wires; 9—stirrer; 10—supports.

Thermochemistry, in any case the thermochemistry of organic compounds, is based on the determination of the heats of combustion (the enthalpies of combustion) carried out with the aid of special, so-called calorimeter bombs in calorimeters of various designs. The most frequently used calorimeter bomb is the Berthelot bomb. The schematic of a simple water calorimeter with a different type of bomb is given in Fig. 2.11. A certain amount of a substance to be combusted is placed in a cup *2*. The bomb *1* itself is a robust container made of steel in which a considerable oxygen pressure is produced (about 24-40 atm). The bomb is immersed in water *4*. The stirrer *9* is switched on and the change in temperature of water in the calorimeter is determined—this is the preliminary stage. Upon completion of this stage the substance is burned with the aid of an electric wire *8* and the temperature change at the principal stage is followed. After appropriate corrections are made these measurements allow one to find the increase in the calorimeter temperature resulting from the evolution of heat upon combustion of the substance.

The heat of combustion is determined in the bomb at constant volume, $Q_v = \Delta U$. It is usually recalculated to constant pressure, obtaining $Q_p = \Delta H$ (see page 69).

The procedure of calorimetric measurements allows one to obtain results with a high degree of accuracy. Let us consider some examples of the heats of combustion:

$$\begin{array}{ll}
H_2+\frac{1}{2}O_2=H_2O\ (\text{liq}) & \Delta H^\circ_{298}=-68317.4\ \text{cal/mole}=\Delta H_1 \\
H_2+\frac{1}{2}O_2=H_2O\ (\text{vap}) & \Delta H^\circ_{298}=-57797.9\ \text{cal/mole} \\
C_{\text{graphite}}+O_2=CO_2 & \Delta H^\circ_{298}=-94052\ \text{cal/mole}=\Delta H_2 \\
CH_4+2O_2=CO_2+2H_2O\ (\text{liq}) & \Delta H^\circ_{298}=-212{,}800\ \text{cal/mole}=\Delta H_3
\end{array} \tag{2.103}$$

Before turning to the use of these data let us once again speak of the symbol ΔH. The heats of reactions depend, as has already been said, on the conditions under which reactions are carried out and on the states of the reactants. As an example of the dependence on the state may be cited the first two reactions in (2.103), whose enthalpies differ by the enthalpy of vaporization of one mole of water. An interesting example is the reaction of formation of hydrogen iodide:

$$H_2 + I_2\ (\text{sld}) = 2HI \qquad \Delta H = +\ 12.4\ \text{kcal}$$

and

$$H_2 + I_2\ (\text{vap}) = 2HI \qquad \Delta H = -\ 2.48\ \text{kcal} \tag{2.104}$$

Here the difference—the value of the enthalpy of sublimation of iodine ($\Delta H_{\text{subl}} = 14.88$ kcal/mole)—leads to the transformation of the endothermic to the exothermic reaction.

The heats of reactions are substantially dependent on the temperature and, to a lesser degree, on the pressure. Let us compare the heats referred to identical conditions. For the sake of convenience and in order to avoid possible errors we shall refer the heats to definite *standard conditions*. In other words, it is presumed that the reaction occurs between individual (pure) substances, which are in certain standard states. The standard states of solid and liquid substances are their stable states under ordinary conditions (at a pressure of 1 atm); for example, iodine is solid, bromine is liquid, carbon is graphite, sulphur forms orthorhombic crystals, water is liquid (though the vaporous state of water is sometimes used as the standard state), etc. Somewhat more complicated is the choice of the standard state for gaseous substances. This is, first, the pressure of a given gas equal to 1 atmosphere and, second, the condition that the gas obeys the equation of state of an ideal gas. Thus, a gas in its standard state is an ideal gas. In practice, corrections for non-ideality must be introduced into the heats determined, of course, for real gases.* True, these corrections are often small. The heats determined in this way are called *standard heats* and are designated by the zero superscript, ΔH°, which stands for standard. The standard state and, hence, the standard heat may, generally speaking, refer to any temperature, including the absolute zero. However, most present-day data of thermochemical tables refer to 25°C and 298.15°K. Hence, the designation ΔH°_{298}; the hundredths of a degree in the temperature subscript are omitted. If we take, for example, the second reaction in (2.103), then ΔH°_{298} signifies the heat effect of the following conversion: 1 mole of hydrogen at 1 atm pressure and a temperature of 298.15°K and 0.5 mole of oxygen under the same conditions form 1 mole of water vapour also at 1 atm and 298.15°K; besides, all the reactants are, by convention, in an ideal gas state. In this example, the standard state of water vapour (1 atm, 298.15°K) is far from the physically real state since the equilibrium pressure of water vapour at the given temperature is only 0.0312 atm and the real vapour cannot be compressed to 1 atm. It should be kept in mind that this conceived compression refers not to a real vapour but to an ideal gas.

The introduction and use of standard heats allows one to represent the heats as the algebraic sum not of the partial molar functions, as in Eq. (2.86), but simply of the molar values of the enthalpies or internal energies of the reactants and products in their standard states. This also makes it possible to use (in the Kirchhoff formula; see Sec. 2.7) the molar heat capacities of pure substances instead of the partial heat capacities.

Using the heats given in Eq. (2.103), let us determine, in accordance with Hess's law, the heat of formation (the enthalpy) of methane. First, we draw a scheme representing two paths for the preparation of the final products: the direct path of preparing H_2O and CO_2 from the reactants and the path involving the intermediate formation of methane (Fig. 2.12). As seen from the scheme, there must exist the equality $2\Delta H_1 + \Delta H_2 = \Delta H_x + \Delta H_3$ or $\Delta H_x = -68317.4 \times \times 2 - 94{,}052 + 212{,}800 = -17{,}887$ cal/mole $CH_4 = \Delta H^\circ_{298}$. Such is the *enthalpy of formation* of methane from its elements, which are in their standard states.* In a similar way we can determine the enthalpies of formation of compounds from simple substances. These quantities are the principal thermochemical characteristics of compounds and are assembled into tables, an example of which can be found in any handbook. The enthalpies of formation of compounds from simple substances play a significant role in the theory of molecular structure. They are used to determine the bond energies in molecules. Thus, knowing the enthalpy of vaporization of graphite or, what is the same thing, the enthalpy of formation of gaseous carbon C_{gas} (it has been found to be equal to $\Delta H^{\circ}_{298} = 171.3$ kcal/mole) and, for example, the enthalpy of dissociation of the hydrogen molecule into atoms**,

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* The methods used to introduce corrections will be described in Chapter 5 (Sec. 5.13).

$$H_2 \rightarrow H + H \qquad \Delta H^{\circ}_{298} = 104.18 \text{ kcal/mole} \qquad (2.105)$$

one can determine, with the aid of Hess's law, the enthalpy of formation of methane not from simple substances but from atoms, $\Delta H = -398.0$ kcal/mole. Since the CH_4 has four C—H bonds, it follows that one-fourth of the value given will constitute, on the average, the enthalpy of formation of one mole of one C—H bond, $\Delta H^{\circ}_{298} = -99.5$ kcal/mole.

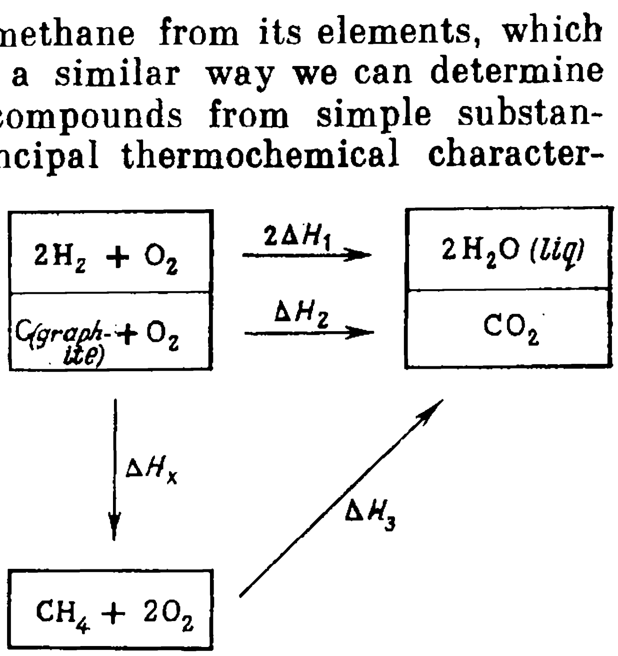

Fig. 2.12. Determining the enthalpy of formation of methane.

In practice, use is almost exclusively made of the enthalpy of a reaction, i.e., the heat effects at constant pressure. However, the heats at constant volume are experimentally determined, for example, on combustion in a calorimeter bomb: $Q_v = \Delta U$. Besides, having at our disposal tabulated values of ΔH, it is useful to know how they can be recalculated to ΔU. As seen from Eqs. (2.91) and (2.92), the difference between $\Delta U = Q_v$ and $\Delta H = Q_p$ is due to the work of expansion or compression being done at constant pressure in the second case. If the reaction proceeds between substances in the condensed state, i.e., solid or liquid substances, the difference between ΔU and ΔH may be practically neglected because of small volumes and low absolute values of volume changes. But this does not apply to reactions involving gaseous substances. We shall now write down such a reaction in a general form:

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* The author recommends that in solving problems according to Hess's law the reader should first draw schemes similar to that given in Fig. 2.12. After the reader has acquired some experience he may pass over to a purely algebraic method or any other method.

** The determination of such data is based on spectroscopic techniques.

$$\nu_1 B_1 + \nu_2 B_2 + \ldots = \nu_1' B_1' + \nu_2' B_2' + \ldots \tag{2.106}$$

where ν_i are the stoichiometric coefficients; B_i are the symbols for the gaseous reactants and products. Introducing the molar volume $\underline{v}$ for all (ideal) gases, we write the volume change for the reaction:

$$\Delta \underline{v} = \underline{v}(\nu_1' + \nu_2' + \ldots - \nu_1 - \nu_2 - \ldots) = \underline{v} \sum \nu_i \tag{2.107}$$

where $\sum$ signifies an algebraic sum. Employing the ideal-gas equation, we obtain:

$$\Delta v = \frac{RT}{p} \sum \nu_i \tag{2.108}$$

Finally, substituting Δv into Eq. (2.92), we find that

$$\Delta H = \Delta U + p\Delta v = \Delta U + RT \sum \nu_i \tag{2.109}$$

According to relation (2.107), for a reaction with the same number of moles of the gaseous reactants and products, for example, for the reaction $N_2 + O_2 = 2NO$, $\sum \nu_i = 0$ and $\Delta H = \Delta U$, i.e., the heats at constant pressure is equal to that at constant volume. With $\sum \nu_i$ different from zero the difference may reach substantial values. For example, for the synthesis of ammonia, $N_2 + 3H_2 = 2NH_3$, the value of $\Delta H^\circ_{298} = -22{,}080$ cal per 2 moles of NH_3, $\sum \nu = -2$ and hence,

$$\Delta U^\circ_{298} = \Delta H - RT \sum \nu_i = -22{,}080 + \\ + 2 \times 1.987 \times 298 = -20{,}880$$

In other words, upon formation of two moles of ammonia under the conditions of constant volume the amount of heat evolved is approximately 1200 cal less than that at constant pressure. One should clearly know the source of an extra amount of heat at constant pressure. The formation of ammonia is associated with a decrease in volume of the system, which is acted on by an external force. This pressure produces work on the system, this leading to the appearance of an extra amount of heat. If the exothermic reaction were accompanied by an increase in the number of moles, the system would do work at constant pressure against the forces of external pressure. In this case, the amount of heat evolved would be lower. We suggest that the reader think over other possible variants.

2.7. Basic Laws of Thermochemistry. The Kirchhoff Equation

Another important thermochemical regularity is the dependence of the heat of reaction on temperature expressed by Kirchhoff's equation. We shall seek the dependence of the integral effect

$$\Delta H_{T,p} = f(T) \tag{2.110}$$

of the reaction

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightarrow \nu'_1 B'_1 + \nu'_2 B'_2 + \ldots$$

Taking account of what has been said in Sec. 2.5 [Eq. (2.89)], we represent the integral heat effect approximately as the algebraic sum of the partial molar enthalpies of the substances in the reaction mixture:

$$\Delta H_{T,\,p} = \nu'_1 \bar{h}'_1 + \nu'_2 \bar{h}'_2 + \ldots - \nu_1 \bar{h}_1 - \nu_2 \bar{h}_2 - \ldots \tag{2.111}$$

Differentiating Eq. (2.111) with respect to temperature at constant pressure, we obtain the following relation:

$$\frac{\partial \Delta H}{\partial T} = \sum_{i'} \nu'_i \left(\frac{\partial \bar{h}'_i}{\partial T} \right)_p - \sum_{i} \nu_i \left(\frac{\partial \bar{h}_i}{\partial T} \right)_p \tag{2.112}$$

where ν'_i are the stoichiometric coefficients for the products and ν_i are the stoichiometric coefficients for the reactants. According to Eq. (2.79), $C_{p,\xi} = (\partial H/\partial T)_{p,\xi}$ expresses the heat capacity of a multicomponent system at constant temperature and composition, and

$$\bar{C}_{pi} = \left(\frac{\partial C_{p,\xi}}{\partial n_{i'}} \right)_{T,\,p,\,n_j \neq n_i} \tag{2.113}$$

will represent the partial molar heat capacity of the *i*th component in the mixture. But with continuous functions the order of differentiation is immaterial, and therefore the partial molar heat capacity may be given as

$$\bar{C}_{pi} = \frac{\partial^2 H}{\partial T\, \partial n_i} = \frac{\partial^2 H}{\partial n_i\, \partial T} = \left(\frac{\partial \bar{h}_i}{\partial T} \right)_{p,\, n_j \neq n_i} \tag{2.114}$$

that is, it is equal to the derivative of the partial molar enthalpy with respect to temperature. Thus, Eq. (2.112) assumes the form

$$\frac{\partial \Delta H}{\partial T} = \sum_{i'} \nu'_i C'_{pi} - \sum_{i} \nu_i C_{pi} \tag{2.115}$$

But in accordance with Euler's theorem on homogeneous functions the sum $\sum_{i'} \nu'_i C'_{pi} = C_{p\,\mathrm{II}}$, i.e., is equal to the heat capacity of the products in the mixture taken in the amounts ν'_1, ν'_2, ..., and $\sum_{i} \nu_i C_{pi} =$

$= C_{pI}$ is the heat capacity of the reactants in the reaction mixture taken in the amounts $\nu_1, \nu_2, \ldots$ moles. Hence, the derivative $\partial \Delta H / \partial T$ equals the difference in heat capacities of the products and reactants, i.e.,

$$\frac{\partial \Delta H}{\partial T} = C_{pII} - C_{pI} = \Delta C_p \tag{2.116}$$

This is Kirchhoff's equation in differential form. Strictly speaking, it contains partial molar heat capacities which are, as a rule, unknown. Therefore, it is better to turn directly to the standard heat, assuming that each substance is in pure form and in its standard state in separate vessels. The required amounts ν_i of the reactants are removed from the vessels, the reactants are mixed in some way and are made to react, and then the reaction products are separated and distributed among separate vessels. We are not interested here in the detailed procedure since the task consists in comparing the thermodynamic properties of the reactants and products in their standard states. Now ΔC_p in Eq. (2.116) is expressed now by the sum of the molar heat capacities of the substances in their standard states rather than of the partial molar heat capacities and

$$\frac{\partial \Delta H^\circ}{\partial T} = \nu_1' \underline{C}_{p_1}'^{\circ} + \nu_2' \underline{C}_{p_2}'^{\circ} + \ldots - \nu_1 \underline{C}_{p_1}^{\circ} - \nu_2 \underline{C}_{p_2}^{\circ} - \ldots = \Delta C_p^\circ \tag{2.117}$$

Multiplying then by ∂T

$$\partial \Delta H_T^\circ = \Delta C_p^\circ \, \partial T \tag{2.118}$$

we use an indefinite integral and obtain the integral Kirchhoff equation:

$$\Delta H_T^\circ = \int \Delta C_p^\circ \, dT + \Delta H_J \tag{2.119}$$

where ΔH_J is the integration constant which requires special calculations.

The Kirchhoff equation is used in three approximations. In the first, crude approximation, it is assumed that

$$\Delta C_p = 0 \tag{2.120}$$

that is, the total heat capacities of the products and reactants are assumed to be equal. Then, from Eq. (2.116) it follows that

$$\Delta H_{T_2} = \Delta H_{T_1} = \text{const} \tag{2.121}$$

that is, the heat is considered to be independent of temperature. This approximation is used in the derivation of some simple formulas, for example, in the approximate integration of the isobaric curve for the reaction. In the second, more accurate approximation the difference in the heat capacities is assumed to be a constant quantity, i.e.,

$$\Delta C_p = \text{const} \tag{2.122}$$

Then ΔC_p may be taken outside the integral sign and, for example, for Eq. (2.119) we obtain the following formula of the second approximation:

$$\Delta H_T^\circ = \Delta H_J + \Delta C_p^\circ T \tag{2.123}$$

Here it is appropriate to make the following remark. Instead of calculating the indefinite integral of (2.119), the integration is often carried out from 0 to T and ΔH_0 is written instead of the constant ΔH_J. In such a case, the reservation is made that ΔH_0 is devoid of the physical significance of the reaction enthalpy at $T = 0$. More correctly, ΔH_0 would have this physical meaning if on integration of Eq. (2.119) use were made of the function $\Delta C_p = f(T)$, which retains its value down to temperatures close to the absolute zero. In the majority of practical cases, however, on integration of Eq. (2.119) use is made of the dependences of heat capacities which are valid for relatively high temperatures and which are unsuitable in the region of the absolute zero. Therefore, in such cases the indefinite integral should be taken and ΔH_J written, assuming this quantity to be only a certain constant suitable for the calculation of ΔH_T within temperature ranges where heat capacity functions are valid.

TABLE 2.1. **Values of Standard Heat Capacities for Reaction (2.124)**

Substance	CH_4	C_2H_4	H_2
$C_{p\,298}^\circ$, cal/deg·mole	8.54	10.41	6.892

Let us consider the calculation, in the second approximation, of the dependence of enthalpy on temperature for the reaction of conversion of methane into ethylene:

$$2CH_4 = C_2H_4 + 2H_2 \tag{2.124}$$

The values of the enthalpies of formation of the reagents are taken from appropriate tables* (for hydrogen this value is zero). Using Hess's law, we find the standard enthalpy of the reaction: $\Delta H_{298}^\circ = 48{,}300$ cal/mole of C_2H_4. The values of standard heat capacities at 298.15°K are also taken from tables; they are given in Table 2.1. On the basis of these data we can write the change in the heat capacity:

$$\Delta C_p^\circ = 10.41 + 2 \times 6.892 - 2 \times 8.54 = 7.11 \text{ cal/deg}$$

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* See, for example, *Chemist's Handbook*, v. I, Goskhimizdat, Moscow, 1963 (in Russian).

We now rewrite Eq. (2.123):

$$\Delta H_T^\circ = \Delta H_J + 7.11\ T \tag{2.125}$$

Further, knowing the reaction enthalpy at 298.15°K, we find ΔH_J:

$$\Delta H_J = 48{,}300 - 7.11 \times 298.15 = 46{,}159$$

Hence, we obtain the final formula of the second approximation:

$$\Delta H_T^\circ = 46{,}159 + 7.11\ T \tag{2.126}$$

Having calculated, for example, the reaction enthalpy at 1000°K, $\Delta H_{1000}^\circ = 52{,}840$, we become convinced that in this particular case it varies rather strongly with temperature—the absorption of heat increases with increasing temperature. This is associated with the high heat capacity of the reaction products and also with the fact that as the temperature increases there also increases the difference in the amount of heat required for heating the products and reactants to a given temperature.

The third, most accurate approximation in the use of the Kirchhoff equation takes account of the dependence of ΔC_p on temperature. It should be noted that the situation is far from satisfactory with the theory of heat capacity, especially in the case of gases and liquids. Therefore, the most reliable way consists in using empirical formulas. Attempts are being made to describe the experimental data of heat capacities at various temperatures by means of a temperature power series; depending on the desired accuracy, use is made of series with different numbers of terms. In a general case,

$$C_p = a + bT + cT^2 + \dots \tag{2.127}$$

As an example, let us note that Lewis and Randall in the first edition of their famous book *Thermodynamics* recommended using the same formula consisting of two terms for a number of gases (N_2, O_2, NO, CO):

$$C_p = 6.5 + 0.001\ T\ \text{(cal/deg·mole)} \tag{2.128}$$

and a somewhat different one for hydrogen:

$$C_p = 6.5 + 0.0009\ T \tag{2.129}$$

More accurate are formulas containing three terms; for example, for H_2:

$$C_p^\circ = 6.9469 - 0.1999 \times 10^{-3}\, T + 0.4808 \times 10^{-6}\, T^2\ \text{(cal/deg·mole)}$$
$$(\Delta T = 300 - 1500\ \text{K})$$

and for CH_4:

$$C_p^\circ = 3.422 + 17.845 \times 10^{-3}\, T - 4.165 \times 10^{-6}\, T^2\ \text{(cal/deg·mole)}$$
$$(\Delta T = 291 - 1500\ \text{K}) \tag{2.130}$$

A tendency has lately been observed to use series including the temperature raised to a negative power: the inverse temperature:

$$C_p = a + bT + cT^2 + c'T^{-2} \tag{2.131}$$

Here the constants a, b, c differ from the analogous quantities in Eq. (2.127). As a reference and illustrative example we give here the table borrowed from the second edition of the book by Lewis

TABLE 2.2. **Equations for Heat Capacity, (cal/deg·mole)**

All monatomic gases with no appreciable electronic excitation: $C_p^\circ = 4.97$	
Other gases (applicable 298 to 2000°K)	
S	$C_p^\circ = 5.26 - 0.10 \times 10^{-3}\,T + 0.36 \times 10^5\,T^{-2}$
H_2	$C_p^\circ = 6.52 + 0.78 \times 10^{-3}\,T + 0.12 \times 10^5\,T^{-2}$
O_2	$C_p^\circ = 7.16 + 1.00 \times 10^{-3}\,T - 0.40 \times 10^5\,T^{-2}$
N_2	$C_p^\circ = 6.83 + 0.90 \times 10^{-3}\,T - 0.12 \times 10^5\,T^{-2}$
S_2	$C_p^\circ = 8.72 + 0.16 \times 10^{-3}\,T - 0.90 \times 10^5\,T^{-2}$
CO	$C_p^\circ = 6.79 + 0.98 \times 10^{-3}\,T - 0.11 \times 10^5\,T^{-2}$
F_2	$C_p^\circ = 8.26 + 0.60 \times 10^{-3}\,T - 0.84 \times 10^5\,T^{-2}$
Cl_2	$C_p^\circ = 8.85 + 0.16 \times 10^{-3}\,T - 0.68 \times 10^5\,T^{-2}$
Br_2	$C_p^\circ = 8.92 + 0.12 \times 10^{-3}\,T - 0.30 \times 10^5\,T^{-2}$
I_2	$C_p^\circ = 8.94 + 0.14 \times 10^{-3}\,T - 0.17 \times 10^5\,T^{-2}$
CO_2	$C_p^\circ = 10.57 + 2.10 \times 10^{-3}\,T - 2.06 \times 10^5\,T^{-2}$
H_2O	$C_p^\circ = 7.30 + 2.46 \times 10^{-3}\,T$
H_2S	$C_p^\circ = 7.81 + 2.96 \times \cdot 10^{-3}\,T - 0.46 \times 10^5\,T^{-2}$
NH_3	$C_p^\circ = 7.11 + 6.00 \times 10^{-3}\,T - 0.37 \times 10^5\,T^{-2}$
CH_4	$C_p^\circ = 5.65 + 11.44 \times 10^{-3}\,T - 0.46 \times 10^5\,T^{-2}$
C_2H_2	$C_p^\circ = 12.13 + 3.84 \times 10^{-3}\,T - 2.46 \times 10^5\,T^{-2}$
TeF_6	$C_p^\circ = 35.33 + 1.62 \times 10^{-3}\,T - 7.00 \times 10^5\,T^{-2}$
Liquids applicable from melting point to boiling point:	
I_2	$C_p^\circ = 19.20$
H_2O	$C_p^\circ = 18.04$
NaCl	$C_p^\circ = 16.0$
$C_{10}H_8$	$C_p^\circ = 19.0 + 97.4 \times 10^{-3}\,T$
Solids applicable from 298°K to melting point or 2000°K:	
C (graphite)	$C_p^\circ = 4.03 + 1.14 \times 10^{-3}\,T - 2.04 \times 10^5\,T^{-2}$
Al	$C_p^\circ = 4.94 + 2.96 \times 10^{-3}\,T$
Cu	$C_p^\circ = 5.41 + 1.50 \times 10^{-3}\,T$
Pb	$C_p^\circ = 5.29 + 2.80 \times 10^{-3}\,T + 0.23 \times 10^5\,T^{-2}$
I_2	$C_p^\circ = 9.59 + 11.90 \times 10^{-3}\,T$
NaCl	$C_p^\circ = 10.98 + 3.90 \times 10^{-3}\,T$
$C_{10}H_8$	$C_p^\circ = -27.7 + 224 \times 10^{-3}\,T$

and Randall* (see Table 2.2). In constructing the dependence $\Delta C_p = f(T)$ one should make use of heat capacity functions of the same form. For example, if dependences of the type (2.121) are taken, then we must write:

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 + \dots \tag{2.132}$$

where, for example, Δa is the following algebraic sum written with account taken of the coefficients of a chemical equation (see page 71):

$$\Delta a = \nu_1' a_1' + \nu_2' a_2' + \dots - \nu_1 a_1 - \nu_2 a_2 - \dots \tag{2.133}$$

and analogous equations can be written for Δb and Δc. Substituting the series (2.132) into Eq. (2.119), we obtain the Kirchhoff calculation formula of the third approximation:

$$\Delta H_T = \Delta H_J + \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 + \dots \tag{2.134}$$

Here, as before, ΔH_J is a constant which is most often determined from ΔH_{298}. In calculations of this kind one can dismiss the separate calculation of ΔH_J, using the definite integral in Eq. (2.119) and assuming, say, $T_1 = 298.15°K$, but in this case the calculation formula would contain the differences of the second and third powers of temperatures, which would be rather inconvenient. In view of this, it is recommended that use be made of formula (2.134) or one similar to it based on expression (2.131), the more so that such equations find further application in calculations of the temperature dependence of the chemical equilibrium (see Sections 5.4 through 5.9). In conclusion, it should be noted that if one is speaking of standard conditions, all the symbols ΔH and C_p should be assigned the zero superscripts; thus, for example, Eq. (2.134) will assume the following form:

$$\Delta H_T^\circ = \Delta H_J^\circ + \Delta a^\circ T + \frac{1}{2}\Delta b^\circ T^2 + \frac{1}{3}\Delta c^\circ T^3 + \dots \tag{2.135}$$

2.8. The Heat Capacity of Solids According to Einstein and Debye

According to the Dulong-Petit law the heat capacities of monatomic solid crystalline substances at fairly high temperatures tend to a limiting value, $C_v \approx 6$ cal/deg·g-atom, and in the region close to absolute zero they vanish i.e., $C_v \to 0$ at $T \to 0$.

These facts were first explained by Einstein, who developed the *quantum theory of heat capacity* on the basis of the quantum theory proposed in 1900 by Max Planck. According to Einstein a crystalline body consists of vibrating atoms, each atom being a three-dimensional harmonic oscillator. Imagine a point (an atom) held in a position of equilibrium (0) by the forces acting on it (Fig. 2.13*a*). If the point is displaced, there arises a force F that tends to return the point to its initial position. In the case of a harmonic oscillator, this force, called the *restoring force*, is considered to be quasi-elastic, i.e., one obeying Hooke's law:

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* Lewis, G. N. and M. Randall, *Thermodynamics*, 2nd edition. Revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Company, Inc., New York, 1961.

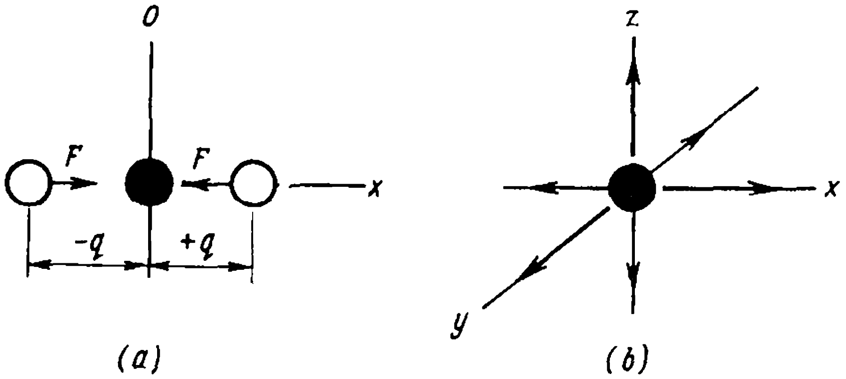

Fig. 2.13. Illustrating the Einstein theory of heat capacity.

$$F = -kq \tag{2.136}$$

According to the laws of classical mechanics, the force (2.136) has a potential and the displacement q is associated with an increase in potential energy of a particle:

$$\varepsilon_{\text{pot}} = \frac{1}{2} kq^2 \tag{2.137}$$

As a result of the displacement, a harmonic oscillation is generated. The moving particle (the atom) will also possess a kinetic energy:

$$\varepsilon_{\text{kin}} = \frac{1}{2} m\dot{q}^2 \tag{2.138}$$

where m is the mass of the particle; $\dot{q} = \partial q/\partial t$ is the velocity of its motion. The frequency of the oscillation generated, ν, depends on the mass m and the force constant k in the following manner:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}, \ \text{s}^{-1} \tag{2.139}$$

According to Planck, the total energy of the oscillator assumes only definite *quantized values**:

$$\varepsilon = \varepsilon_{\text{kin}} + \varepsilon_{\text{pot}} = h\nu \left(\frac{1}{2} + v\right) \tag{2.140}$$

---

* M. Planck did not give the factor $\frac{1}{2}$ but it does not matter in this particular case.

where v is the so-called vibrational quantum number which takes on whole numbers, 0, 1, 2, 3, ..., and h is Planck's constant (the elementary quantum of action); $h = 6.6252 \times 10^{-27}$ erg·sec. The average energy of the oscillator in a crystal increases with increasing temperature, and as $T \to 0$ the energy of the oscillator approaches the so-called *zero-point energy*, $\varepsilon_0 = \frac{1}{2} h\nu$. Einstein was the first to see the relationship between these ideas and the temperature dependence of heat capacity in the region close to absolute zero. According to his viewpoint (1904), a crystal containing N atoms is an assembly of $3N$ harmonic oscillators [or, what is the same thing, N three-dimensional oscillators (Fig. 2.13*b*)], which vibrate at a single frequency ν_0. As a result of calculations (see Chapter 6), the formula was derived which is known as the Einstein function*:

$$C_v = 3R \frac{\left(\frac{\theta_\varepsilon}{T}\right)^2 e^{\theta_\varepsilon/T}}{(e^{\theta_\varepsilon/T} - 1)^2} \tag{2.141}$$

where θ_ε is the Einstein characteristic temperature defined as

$$\theta_\varepsilon = \frac{h\nu_0}{\mathrm{k}} \, [\mathrm{deg}] \tag{2.142}$$

in which k is given by

$$\mathrm{k} = \frac{R}{N_A} = 1.38066 \times 10^{-16} \text{ erg/deg} \tag{2.143}$$

This quantity is called Boltzmann's constant; it is a gas constant referred to one molecule. The Einstein function approximately corresponds to experiment. Indeed, if T tends to zero, then θ_ε/T will tend to infinity, in which case the square of the parenthesis in the denominator of (2.141) is approximated by the power of $e^{2\theta_\varepsilon/T}$:

$$C_v \approx 3R \left(\frac{\theta_\varepsilon}{T}\right)^2 e^{-\theta_\varepsilon/T} \tag{2.144}$$

which tends to zero as $T \to 0$. But if the temperature is high, i.e., $T \to \infty$, then $\theta_\varepsilon/T \to 0$ and $e^{\theta_\varepsilon/T} \to 1$. In this case, the parenthesis in the denominator of Eq. (2.141) is approximated by the fraction θ_ε/T and

$$C_v \to 3R \approx 6 \text{ cal/deg·mole} \tag{2.145}$$

While corresponding to the limiting values, the Einstein function provides, in general, a poor description of experimental data at intermediate temperatures.

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* The Einstein function is readily obtainable from the formulas given in Chapter 6 by proceeding from the partition function of the harmonic oscillator:

$$Q_{\mathrm{vib}} = (1 - e^{-h\nu/kT})^{-1}$$

The Einstein theory was improved by Debye (1912) and also by Born and von Kármán (1913) on the basis of the assumption that the vibrations of oscillators exhibit a broad spectrum of frequencies and not a single frequency ν_0, as in the Einstein theory. Debye proposed that a crystal be treated like a giant molecule possessing many different vibrational frequencies ranging almost continuously from zero up to a maximum value, $\nu_{\max}$:

$$g(\nu) = \text{const}\,\nu^2 \tag{2.146}$$

Expression (2.146) is the density* of distribution of oscillators among frequencies and the product $g(\nu)\,d\nu$ will give the number of oscillators with frequencies from ν to $\nu + d\nu$. Figure 2.14 compares the Einstein and Debye distribution functions. Later, Debye used the Einstein formula (2.141). He integrated it in the interval from $\nu = 0$ to $\nu = \nu_{\max}$, as a result of which he obtained the following expression:

$$C_v = 9R\left(\frac{T}{\theta_D}\right)^3 \int\limits_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2}\,dx \tag{2.147}$$

where $\theta_D = h\nu_{\max}/k$ is called the Debye characteristic temperature; this quantity is, in principle, constant for a given substance, and $x = h\nu/kT$ ($x_{\max} = h\nu_{\max}/kT = \theta_D/T$). Expression (2.147) is usually called the *Debye function*. The integral in it is not taken in an analytical sense; it is evaluated by a numerical method; the values, say, of $C_v/3R$, are assembled into tables (see Appendix 2) in the form of a function of the values of θ_D/T.

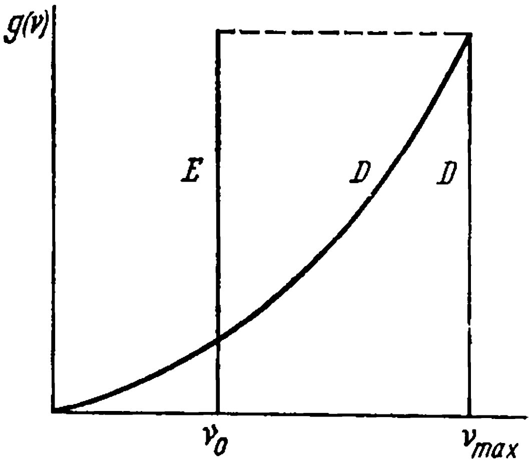

Fig. 2.14. The Einstein and Debye distribution functions.

Let us see to what extent the function (2.147) satisfies the limiting values of heat capacities. If the temperature is high ($T \to \infty$), then x tends to zero, and the integrand tends to $x^2\,dx$. In this case, the integral becomes equal to $x_{\max}^3/3 = 3\,(\theta_D/T)^3$, and $C_v \approx 3R$, i.e., the Dulong-Petit law is valid. At low temperatures ($T \to 0$) the ratio θ_D/T tends to infinity and therefore the following integral can be written instead of the Debye integral:

$$\int\limits_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2}\,dx = \frac{4\pi^4}{15} \tag{2.148}$$

---

* That is, it defines the number of oscillators, which have frequencies in the range from ν to $\nu + 1$.

This integral is evaluated analytically. By virtue of (2.148), the heat capacity in the region of low temperatures is defined thus:

$$C_v = \left(\frac{12}{5} \times \frac{\pi^4}{\theta_D^3} R\right) T^3 = \alpha T^3 \qquad (2.149)$$

Here the term in parentheses is constant for a given substance, and the heat capacity at low temperatures is therefore proportional to the temperature raised to the third power. This is the famous *Debye cube law* (the T^3 law). Calculations show that for temperatures $T \leqslant (\theta_D/16)$ the heat capacity is satisfactorily expressed by the following relation:

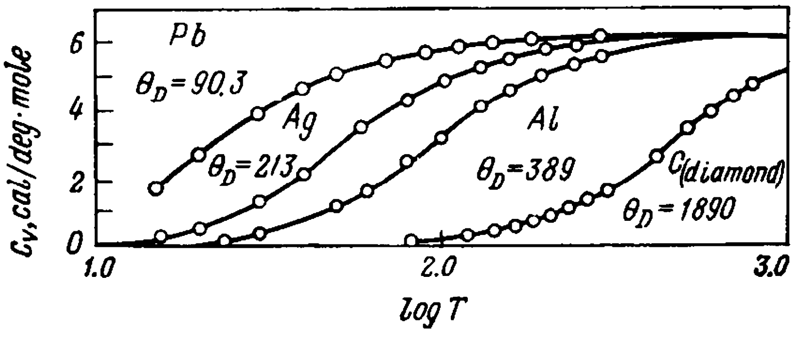

Fig. 2.15. The heat capacities of some simple substances in the solid state: The curves have been calculated from Debye's formula (2.147) with the characteristic temperatures given; the circles represent experimental data.

$$\frac{C_v}{3R} = 77.927 \left(\frac{T}{\theta_D}\right)^3 \qquad (2.150)$$

An important feature of the Debye formula is that it expresses the heat capacity of various elements as a general function of the difference $\log T - \log \theta_D$. Therefore, by constructing graphs of C_v against $\log T$ for various substances one obtains curves having identical shapes but shifted relative to each other in the horizontal direction by an amount $\log \theta_D$. Figure 2.15 shows graphs of the indi-

TABLE 2.3. **The Heat Capacities (cal/deg·g-atom) and Characteristic Temperatures of Some Simple Substances**

Properties of substances	Substance						
	Pb	Au	Ag	Cu	Fe	Al	Diamond
θ_D, °K	90.3	169	213	313	417	389	1890
C_v (25°K)	3.36	1.23	0.75	0.23	0.10	0.11	0.00
C_v (100°K)	5.84	5.10	4.82	3.85	2.88	3.12	0.06
C_v (298°K)	6.41	6.03	6.09	5.85	5.97	5.82	1.45

cated type for some simple substances. It can also be noted that the characteristic temperature $\theta_D = h\nu_{max}/k$ increases with increasing bond forces operative between the atoms in a crystal and decreases with the mass of atoms. Some relevant data are given in Table 2.3. It is also important that the Debye function is applicable to some simple salts, such as NaCl, KCl, CaF_2.

2.9. Equilibrium and Reversible Processes

Formulas that express the work of expansion and compression, (2.10) and (2.25), and others related with these, contain the pressure p. What pressure is this, the gas pressure of the system or the external pressure? We know that these pressures are not equal during the expansion or compression process. The answer may seem paradoxical: both of them. More precisely, all the formulas that have been derived in this chapter for work are valid only if the difference between the pressure in the system and the external pressure is infinitesimal. This condition is written as follows:

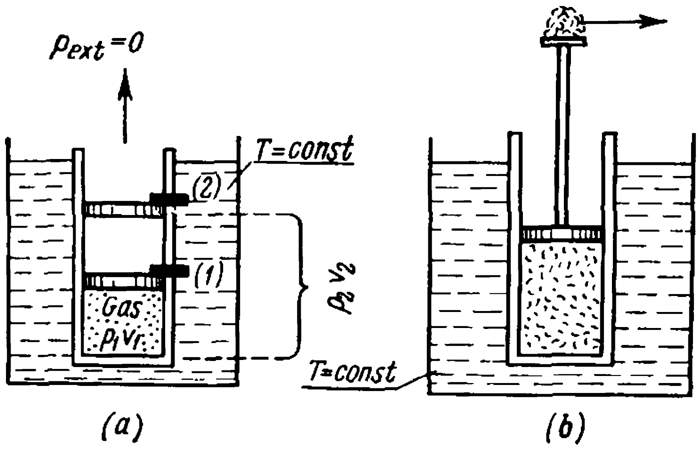

Fig. 2.16. Illustrating the equilibrium process of expansion and compression of a gas.

Gas pressure	External pressure	Process
p	$p - dp$	Expansion
p	$p + dp$	Compression

Such processes are called *equilibrium* or quasistatic. The system is, so to speak, constantly in equilibrium or, accomplishing the process, passes through a continuous series of equilibrium states.

For a more detailed consideration of the conditions under which an equilibrium process takes place and its special features, let us return to the isothermal expansion of an ideal gas. Figure 2.16*a* shows the familiar cylinder with a weightless piston immersed in a thermostat at temperature T. Suppose first that the external pressure is equal to zero and the piston is fixed in position *1*. If the piston is released, the gas will expand and the piston will occupy position *2*; p_1v_1 will then become p_2v_2. Since by condition, the external pressure equals zero and the piston is weightless, it follows that no work will be done in the expansion process, i.e., $W = 0$. Hence, Q will also be equal to zero since $\Delta U = 0$ on the basis of the properties of the ideal gas. The process under consideration is a case of the infinitely non-equilibrium transition.

Figure 2.16*b* shows the same system but in this case the gas pressure is balanced by a weight on the piston. As has been said, the gas will expand if the external pressure is lowered, i.e., if the weights are removed from the piston. Graphically, this process can be pictured as in Fig. 2.17. This figure shows an isotherm for an ideal gas corresponding to Eq. (1.5). The points I and II on the isotherm represent two states with values of $p_1v_1 = p_2v_2$. Let the gas be first in state I at a higher pressure. Remove one weight. The external pressure will immediately fall to a value corresponding to point a, and then the gas will expand more slowly with work being done against the reduced pressure (the horizontal portion ab). At point b after the heat is absorbed and the temperature equilized the system again finds itself in a state corresponding to an ideal isotherm. The work of isobaric expansion that has been done by the gas will evidently be represented by the shaded rectangle with a minor side ab. In state b we again remove one weight. The pressure will again be immediately reduced to point c, this being followed by the expansion of the gas to state d, etc. As a result, the gas will expand to a certain final state II with p_2v_2. The total work done by the gas which is equal to the area under the step-like curve will be smaller than the area under the ideal isotherm calculated from Eq. (2.22). These areas can, however, be brought closer together by removing smaller weights since the steps will then be smaller. In the limit, with infinitesimal weights (it was earlier suggested that the piston be loaded with fine sand and a grain be removed at a time) the step-like curve will merge with the ideal isotherm, and the work done by the gas will become the *maximum work* done by the gas that can be described by Eq. (2.22).

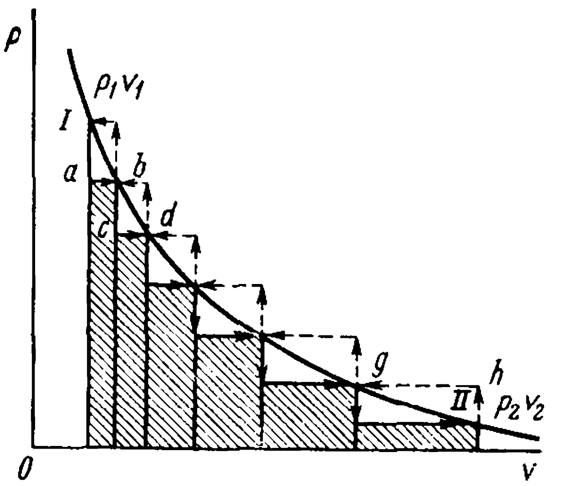

Fig. 2.17. Discussing the equilibrium process of isothermal expansion-compression of a gas.

In conducting the process of compression the piston is first loaded with finite weights. After each of the weights is placed the pressure will immediately increase, say, to point *h*, and then, with a slower compression at constant external pressure, to point *g*. On the whole, the result will be the upper step-like curve, the area under which, being equal to the work consumed for the compression of the gas, will be larger than the area under the isotherm. And again, placing infinitely smaller weights, we see that the step-like curve merges with the smooth isotherm.

On the basis of the example given above we shall formulate the *general conditions* for carrying out equilibrium processes and their properties.

1. An infinitesimal difference between the acting and counteracting forces.
2. The performance of a maximum work in the forward process.
3. The infinitely slow progress of the process associated with the infinitesimal difference between the acting forces and with the infinitely large number of intermediate states.

If we now also compare the forward and reverse processes (expansion and compression, etc.), then additional conditions will arise for equilibrium processes.

4. The absolute work quantities for the forward and the reverse process are equal.
5. The change in the external force by an infinitesimal amount ($p + dp$, $p - dp$) reverses the direction of the process.
6. The paths of the direct and reverse processes coincide.

The above-indicated conditions for the occurrence of equilibrium processes and their specific features partly overlap, but the important point here is that they are of general validity. Strictly speaking, equilibrium processes, which are idealizations of those actually existing, are infeasible in practice. The majority of quantitative calculations in thermodynamics, however, deal exactly with equilibrium processes. In particular, all formulas for the work of expansion and compression in various processes involving ideal gases (Sec. 2.4) can be applied to the conditions under which equilibrium processes are carried out. Further, though equilibrium processes cannot be realized in practice, there is always a possibility, in principle, to approach the equilibrium conditions as close as possible.

Let us now consider the equilibrium conditions for a chemical reaction. In many cases, a chemical reaction if carried out under special conditions, say if we construct a galvanic cell or a storage battery, can proceed with work being done. Thus, in the most frequently used lead storage battery lead and its compounds undergo transformation, as a result of which various systems are formed on the cathode and the anode in the discharged and charged state:

State of storage battery	(−) Cathode	Electrolyte	(+) Anode
Discharged	$PbSO_4$	A solution of sulphuric acid	$PbSO_4$
Charged	Pb		PbO_2

A potential difference arises on the terminals of the charged storage battery. It has the highest value in the opened or compensated state of the battery and is called in this case the electromotive force E. One can imagine the following process of the equilibrium charging-discharging of the storage battery and, hence, of the corresponding chemical conversions: the conversion of lead sulphate to metallic lead on the cathode and the conversion of lead sulphate to lead dioxide on the anode. Figure 2.18 shows the circuit used in the Poggendorff compensation method. The external current source (the dynamo or d-c generator) *1* is connected to the terminals AB of the wire *2* pulled taut along a ruler. The contact *3* slides along the ruler and by moving it we can specify any potential drop E_{ext} on the portion CB. To these points is connected the storage battery *5* through a sensitive galvanometer *4*. By moving the contact one can achieve a complete compensation of the forces ($E_{ext} = E_{sb}$), in which case no current is present in the storage battery. By moving the contact from the point of compensation to right or left we can change the external voltage within the limits: $E_{sb} + dE$ is the charging; $E_{sb} - dE$ is the discharging. This is what corresponds to the equilibrium conditions of the process.

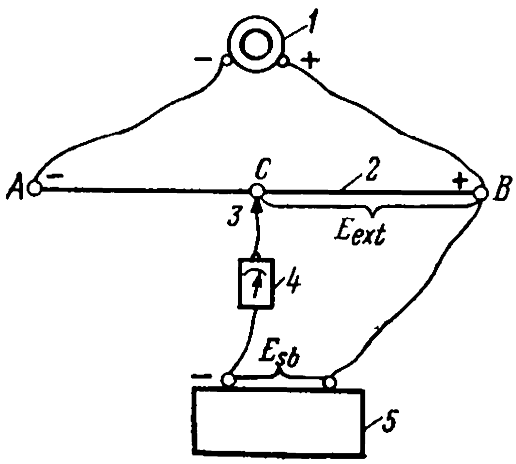

Fig. 2.18. Illustrating the equilibrium process of charging and discharging of a storage battery:

1—external current source; *2*—slide wire; *3*—sliding contact; *4*—galvanometer; *5*—storage battery.

The term "equilibrium process" should not be confused with the term "reversible process", which is also used in thermodynamics. While dealing with equilibrium processes we considered only those systems which are of interest to us, say, a cylinder with a gas or a storage battery. We were not interested in what happens, say, to the thermostat that maintains the temperature of the gas constant. Also, there must be used a device—a mechanism that removes the weights from the piston, etc. In other words, the expansion of the gas involves not only the gas itself in the cylinder, but also all the systems participating in the process. If not only the gas but also all the systems involved undergo equilibrium processes and if they all return to the initial state upon completion of the closed cycle, so that nothing changes in the universe, then such a process is called *reversible.* The concept of the reversible process is more general than that of the equilibrium process. When the system of interest undergoes an equilibrium process, the processes that take place in the other systems involved need not necessarily be equilibrium processes.

Chapter 3

The Second and Third Laws of Thermodynamics

3.1. Spontaneous and Nonspontaneous Processes. Equilibrium

The first law of thermodynamics establishes the equivalency of various forms of energy, in particular, internal energy, heat and work. If a system is isolated from the surroundings, its internal energy remains unchanged. From the standpoint of the first law, any processes are equally probable, in which one form of energy is replaced by an equivalent amount of another form of energy. For example, the lifting of a weight or the compression of a spring at the expense of the internal energy of the surroundings would not contradict the first law of thermodynamics. Why, indeed, wouldn't a stone lying on the ground rise to any height because of the surrounding air being cooled? But it does not. The transfer of heat from a colder to a hotter body would only mean a redistribution of the energy inside the system and would not violate the first law either. We know, however, that water in a vessel placed on the cold gas stove will never boil. To put it otherwise, the first law tells nothing about the possibility and probability of this or that process associated with the conversion of energy or with its redistribution.

Meanwhile, if we examine carefully all the various processes that occur in the universe and also those conducted by man, it will turn out that they can be divided into two essentially different groups. First, there are *spontaneous* processes, i.e., processes that occur of their own accord. No work is done for such processes to occur, and being subjected to specific conditions (so to say, being "harnessed" into a special mechanism), they themselves can do work in an amount proportional to the accompanying change. Examples of spontaneous processes are the following: the mixing of gases; the passage of heat from a hot body to a cold one; the conversion of the energy of a charged storage battery into heat, etc.

If we try to reverse the direction of spontaneous processes, we shall find that this is not that simple. In this case, we are dealing with *nonspontaneous processes*. They do not proceed of their own accord. For such processes to be accomplished, work has to be expended in an amount proportional to the accompanying change. This may be exemplified by the separation of a mixture of gases into its components, the transfer of heat from a cold body to a hot one, and the charging of a storage battery at the expense of heat.

As an example of a spontaneous chemical conversion, let us consider the dissolution of zinc in a solution of cupric sulphate ($CuSO_4 \times \times 5H_2O$). As known, when a zinc stick is dipped into the solution indicated, it becomes covered with a copper layer, i.e., a spontaneous displacement of copper occurs:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad (3.1)$$

which is accompanied by the evolution of heat ($\Delta H < 0$). The process will not proceed in the reverse direction due to the absorption of heat—it is nonspontaneous. But another method can be suggested for carrying out the reaction: the zinc stick is dipped in a solution of $ZnSO_4$ and the copper stick in a solution of $CuSO_4$ (this is the Daniell cell). The solutions must be separated by a porous partition which will prevent them from mixing (Fig. 3.1). Experiment shows that a potential difference arises between the metals (the electrodes). If they are connected by a wire, a current will flow, which can be used with the aid of an electric motor to perform work. Simultaneously, the zinc will dissolve and the metallic copper will separate from the solution. Thus, reaction (3.1) will take place in the cell, i.e., the spontaneous process in this case is doing work.

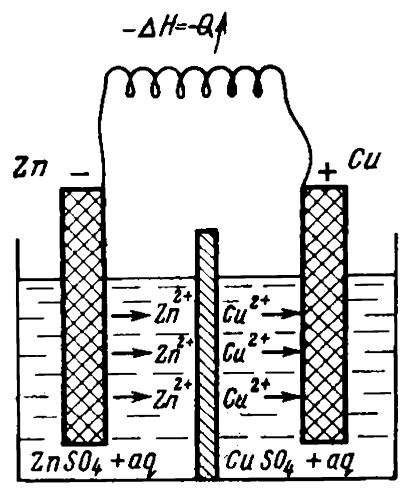

Fig. 3.1. Schematic of the Daniell cell.

To bring about the reverse nonspontaneous process, the deposition of zinc and the dissolution of copper

$$Zn^{2+} + Cu = Zn + Cu^{2+} \qquad (3.2)$$

an external source of electric energy and a circuit (say, the circuit shown in Fig. 2.18) will be needed.

Spontaneous processes bring the system to a state of equilibrium in which the forces responsible for the processes are balanced. For example, the pressure, temperature* and concentration become equilibrated. In a state of equilibrium no visible (macroscopic) changes occur in the system. What is of primary interest to us is the state of *stable equilibrium*, when any slight influence on the system will bring about only a slight change in it. Here an analogy may be drawn with mechanics (Fig. 3.2). The action of small forces on a ball being in a stable equilibrium in a potential well and having a minimum value of potential energy can cause only a small displacement of it. In chemistry, an example of stable equilibrium is the equilibrium of a reversible reaction:

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* Compare with Chapter 2, Sec. 2.1.

$$N_2+O_2 \rightleftharpoons 2NO \tag{3.3}$$

when at a sufficiently high temperature there are attained certain (equilibrium) concentrations (c_i) of the reactants which obey the law of mass action:

$$\frac{c^2_{NO}}{c_{N_2}c_{O_2}}=K_c \tag{3.4}$$

Here a slight change in the conditions—the pressure or temperature—will cause only small changes in the concentration. The equilibrium of the reaction at constant temperature is also associated with the minimum value of energy (free energy).

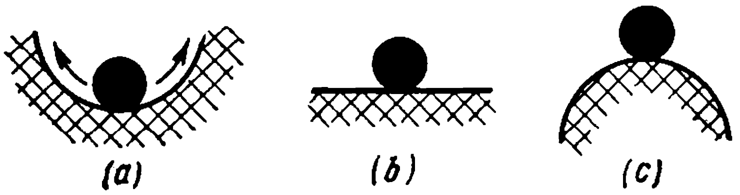

Fig. 3.2. Examples of mechanical equilibrium:
a—stable; b—indifferent; c—unstable.

In thermodynamics, one can also find analogies with other kinds of mechanical equilibrium—indifferent and unstable. We know that a mixture of hydrogen and oxygen can remain unchanged for an indefinite period of time under ordinary conditions.* The equilibrium in this case is, however, unstable since a slight effect, say an electric spark or the introduction of a piece of sponge platinum (a catalyst) will be enough for the reaction of formation of water to occur with an explosion. It is as if we pushed the ball from the top of the sphere (Fig. 3.2*c*).

An example of indifferent equilibrium is the equilibrium between a liquid and its saturated vapour. As long as there exist the vapour and the liquid their relative amounts are neutral (indifferent) just as the position of the ball on a plane (Fig. 3.2*b*).

In Chapter 2 (Sec. 2.9) we considered the concept of equilibrium processes in which systems, while undergoing a change at an infinitely slow rate, pass through a succession of equilibrium states. In a certain sense (see pages 94-95) equilibrium processes may be regarded as being intermediate between spontaneous and nonspontaneous processes. So we see that there are three major classes of processes: spontaneous, equilibrium, and nonspontaneous processes.

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* It can even be compressed and expanded within certain limits in accordance with the gas laws.

The second law of thermodynamics establishes certain general criteria of the spontaneous and nonspontaneous change of the system (processes) and also criteria of equilibrium.

3.2. Various Statements of the Second Law of Thermodynamics

The second law of thermodynamics originated on the basis of a study of the principles of operation of heat engines designed for the conversion of heat into work. The founder is the French military engineer Carnot who published* in 1824 a book entitled "Reflections on the Motive Power of Heat". According to Carnot, for the heat engine to operate in cycles, i.e., for an unlimited amount of heat to be converted into work, at least two heat reservoirs are required, one at a lower temperature and the other at a higher temperature. Carnot's ideas were expounded and developed further mathematically by Clapeyron (1834), who was also the first to propose a graphical representation of the famous Carnot cycle consisting of two isothermal and two adiabatic steps for an ideal gas (Fig. 3.3). This cycle is called the *ideal heat engine*. The efficiency of the Carnot cycle and, in general, the maximum possible efficiency of the heat engine, can be expressed by the following relation, irrespective of the nature of the working substance:

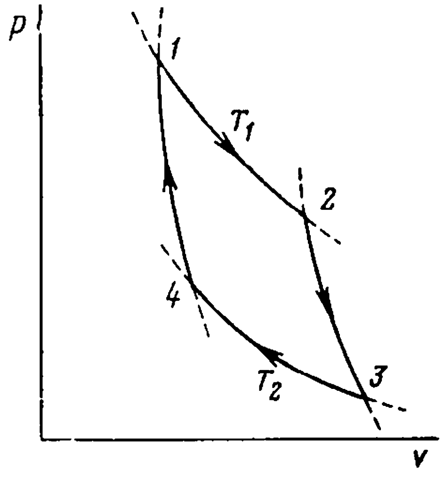

Fig. 3.3. Carnot cycle; pressure-volume diagram:

On the isotherm *1-2* the gas absorbs heat Q_1 from the hot reservoir, and on the isotherm *3-4* it transfers heat Q_2 to the cold reservoir. The processes *2-3* and *4-2* are adiabatics. The difference $Q_1 - Q_2$ is converted to work equal to the area of the cycle *1-2-3-4*.

$$\eta_{\max} = \frac{Q_1 - Q_2}{Q_1} = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{3.5}$$

where Q_1 is the heat received by the working substance from the heat reservoir at temperature T_1; Q_2 is the heat given to the heat reservoir at temperature T_2. The difference $Q_1 - Q_2$ is converted into work.

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* S. Carnot, *Reflexions sur la puissance motrice du feu*, Bachelier, 1824. Carnot used the term "motive power" in the same sense that we use "work".— *Tr.*

According to Eq. (3.5), the efficiency of the heat engine is proportional to the temperature difference $T_1 - T_2$. It may be equal to unity provided that the temperature of the cold reservoir is equal to absolute zero. The efficiency increases also with increasing temperature of the hot reservoir (or of the working substance). It is for this reason that in modern turbines attempts are made to increase the vapour temperature as much as possible, bringing it up to the "red heat" temperature.

All the foregoing, including formula (3.5), may be regarded as the formulation of the second law. The historical paradox is that this formulation had appeared before the law of conservation of energy and the first law of thermodynamics were enunciated. The point is that Carnot and Clapeyron adhered to the caloric theory, according to which heat was treated as a special weightless fluid, the caloric or thermogen, which is contained in bodies in a larger or lesser amount, this being responsible for the temperature of the body. First, this concept implied the law of conservation since the fluid was treated as indestructible. Second, work could be done by the caloric only when it was transferred from a hotter to a cooler body, i.e., as though it was transferred from a higher to a lower level, analogously to the flow of water in communicating vessels.

At a later time, when the caloric theory had to be completely rejected, it became necessary to reconsider the Carnot-Clapeyron ideas. This was done by Clausius (1850) and Lord Kelvin (William Thomson) (1851). Accordingly, we know two formulations of the second law which are called classical.

The Clausius statement is as follows: *It is impossible to construct a machine which is able to convey heat by a cyclical process from one reservoir (at a lower temperature) to another at a higher temperature.*

Figure 3.4 shows schematically the operation of an imaginable device which we shall tentatively call the "anti-Clausius" machine. Almost at the same time there appeared another formulation of the second law, that of Lord Kelvin (W. Thomson): *It is impossible to construct a machine that, operating in a cycle, will only extract heat from a hot reservoir and convert it into an equivalent amount of work.*

Figure 3.5 illustrates the operation of a device which we shall call the "anti-Kelvin" device, i.e., one which is impossible to construct from the viewpoint of the given statement of the second law.

Why are the Clausius and Kelvin statements dealing with a cyclic process? It is because, for example, upon a single expansion of an ideal gas obeying the isotherm *1-2* (see Fig. 3.3) there is possible, in principle, a complete conversion of heat into work [recall relation (2.25), where $Q_T = W_T$].

But the gas cannot be expanded infinitely, and for operations producing the second, etc., "portions" of work to be repeated the gas must be compressed. If the gas is compressed at the same temperature

T_1, i.e., according to the isotherm *2-1* (see Fig. 3.3), no gain in work will be obtained. Therefore, in the Carnot cycle the gas is expanded adiabatically from state *2* to state *3*, its temperature being lowered to T_2. Compression at T_2 requires the expenditure of a lesser amount of work [formula (2.25)], and therefore, on the whole, a gain in work is obtained, which is equal to the area of the cycle *1234*.

The Kelvin statement coincides, in essence, with the Carnot statement since it implies the possibility of conversion of $Q_1 - Q_2$ into work if Q_1 is the heat taken from the hot reservoir and Q_2 is the heat given to the cold reservoir. This formulation is therefore also called the *Kelvin-Carnot statement.*

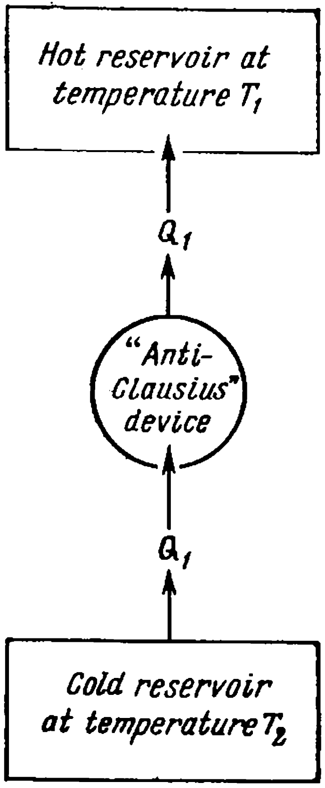

Hot reservoir at temperature T_1
Q_1
"Anti-Clausius" device
Q_1
Cold reservoir at temperature T_2

Fig. 3.4. The "anti-Clausius" device absorbs heat Q_1 from the cold reservoir and transfers it to the hot reservoir.

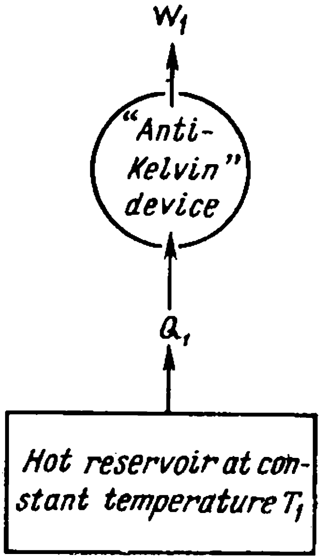


Fig. 3.5. The "anti-Kelvin" device takes heat Q_1 from the hot reservoir and transforms it by a cyclical process into an equivalent amount of work.

Here mention can be made of the problem of the energy source which is of vital importance for the further progress of our civilization. It might seem that man has at his disposal enormous reserves of energy in the form of the heat (internal energy) of tropical seas. We know that cooling of 1 litre of water by one degree is equivalent to 1 kcal and 427 kgm of work. The second law, however, restricts the possibility of using this energy—even if we had the required second heat reservoir at a lower temperature in lower layers of water, the difference $T_1 - T_2$ would prove to be small and the work produced expensive. Attempts in this direction are nevertheless being made.

The Clausius and Kelvin-Carnot statements of the second law are equivalent. Suppose again that we have two thermal reservoirs with temperatures $T_1 > T_2$ and the "anti-Clausius" device connected to them (Fig. 3.6), which is supposed to take the heat Q_2 from the cold reservoir (at a lower temperature T_2) and give it all to the hot reservoir at T_1. These heat reservoirs are also connected to a heat engine, which is considered possible from the standpoint of the second law. This heat engine is designed so that it takes the heat Q_1 from the hot reservoir and transfers to the cold reservoir the heat Q_2 taken from it by the "anti-Clausius" device. Thus, the cold reservoir is brought back to its initial condition, and the net result of the operation of the device is the conversion of the entire amount of heat $Q_1 - Q_2$ taken from the hot reservoir into work. This contradicts the Kelvin-Carnot formulation. Classical thermodynamics developed in the second half of the 19th century was based exactly on the above formulations of the second law. It was found, however, that these postulates alone did not suffice to build the complete theoretical framework of thermodynamics. Recourse had to be made to additional physical images, which are not necessarily physically real. For example, recourse was made to the concept of an ideal gas. Additional postulates were also required.

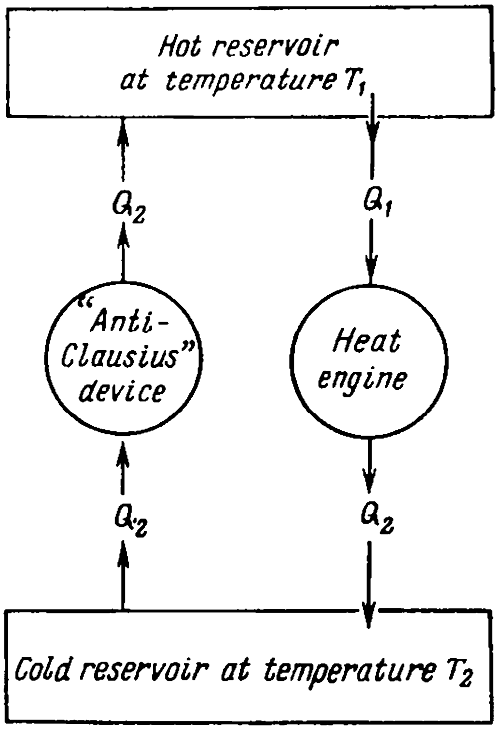

Hot reservoir at temperature T_1
Q_2
Q_1
"Anti-Clausius" device
Heat engine
Q_2
Q_2
Cold reservoir at temperature T_2

Fig. 3.6. A proof of the equivalency of the Clausius and Kelvin-Carnot formulations of the second law of thermodynamics.

Therefore, searches for a general principle that alone (plus the first law) would suffice for building the entire system of thermodynamics by purely logical and mathematical means are understandable. Perhaps the most successful attempt was due to C. Carathéodory. In 1909 he worked out what has come to be known as the *principle of adiabatic unattainability*: *In the neighbourhood of every equilibrium state of a thermodynamic system there are states that cannot be reached from the first state along any adiabatic path, either equilibrium or spontaneous.*

This principle may be regarded as one of the formulations of the second law of thermodynamics. As shown by Carathéodory, the unattainability principle and the mathematical theorem* worked out by him can be used to build thermodynamics by purely logical and mathematical means, without recourse to additional concepts. We shall not make use of the path mentioned since it requires an unwieldy mathematical apparatus. However, we intend first to demonstrate that the principle of adiabatic unattainability is consistent with the classical formulations of Clausius and Kelvin. Second, we shall take advantage of the results that stem from this principle.**

Let us consider a simple system whose state is governed by two variables, say, the volume v and the pressure p. The equilibrium states of such a system will be represented, as known, by points on the p-v diagram. Consider two equilibrium isothermal paths at T_1 and T_2 (Fig. 3.7). Let the system absorb heat ($Q > 0$) when the representative point moves along the isotherm from left to right, i.e., as is the case on the isotherm of an ideal gas. We conduct an equilibrium adiabatic process (path) from an arbitrary state A on the isotherm at temperature T_1. Let this path intersect the lower isotherm at temperature T_2 at point B. Let us choose, on the isotherm, at temperature T_1, an arbitrary state to the left of state A. Assume now that there exists an adiabatic path (process), an indifferently equilibrium or spontaneous, which transfers the system from B to C. This path is depicted as spontaneous in Fig. 3.7. The manner in which it is drawn stresses that it has one direction and also that the points on this path do not lie in the p-v plane since they do not correspond to any equilibrium state of the system under consideration.

Let us now examine the non-equilibrium cycle $ABCA$ as a whole. The absorption of heat by the system during this cyclic process occurs only on the isotherm portion CA; it equals Q_{CA}. The other portions of the cycle are adiabatic, and therefore

$$Q_{\text{per cycle}} = Q_{CA} \tag{3.6}$$

The change in internal energy of the system upon completion of the cycle is zero since the system returns to the initial state, i.e.,

$$\Delta U = 0 \tag{3.7}$$

---

* This theorem is concerned with the question of the presence of an integrating factor in some differential relations (Pfaffian equations).

** Strictly speaking, the Carathéodory principle does not lead to the law of the increase of entropy. In order to choose between alternative possibilities that follow from the principle of the increase or decrease of entropy it is necessary to resort to data obtained by experiments, for example, the transfer of heat from a hotter body to a colder body.

Thus, according to the first law of thermodynamics (2.17) we find that

$$W_{\text{per cycle}} = Q_{\text{per cycle}} \tag{3.8}$$

In other words, the net result of the operation of the cycle is the extraction of the heat Q_{CA} from the heat reservoir at temperature T_1 and the conversion of this heat into an equivalent amount of work, which contradicts the Kelvin-Carnot formulation. The supposed adiabatic path BC is therefore also impossible, i.e., the state C cannot be attained from the state B by means of some adiabatic process. Analogously, we can prove that the Carathéodory principle is equivalent to the Clausius formulation.

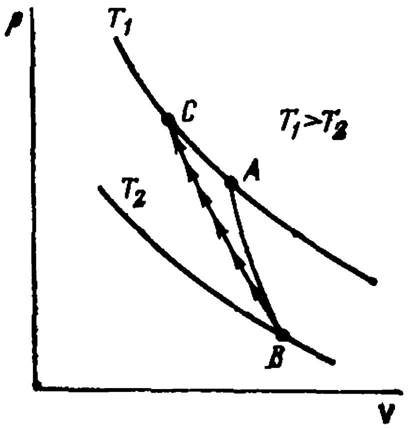


Fig. 3.7. A proof of the agreement between the Carathéodory principle of adiabatic unattainability and the classical formulations of the second law of thermodynamics.

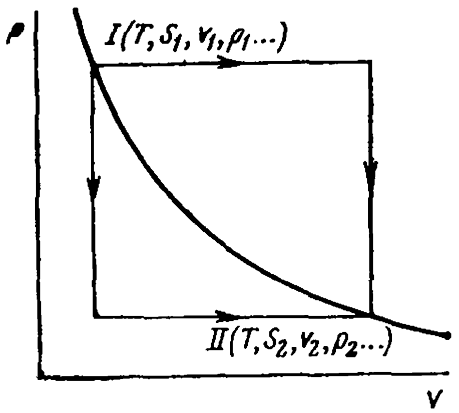


Fig. 3.8. Two states of an ideal gas with equal temperatures but different entropies, S_1 and S_2.

Both the classical formulations and the Carathéodory unattainability principle lead to the establishment of the most important property of the system—the entropy.* At this point we shall not consider the paths that prove its existence. One of these paths is not very rigorous and the other, being associated with the unattainability principle, requires cumbersome mathematical computations. We shall adopt, as a postulate and the basic formulation of the second law of thermodynamics, the following statement: *there exists a certain extensive property of a system, S, called the entropy, whose change is connected with the heat absorbed and the temperature of the system in the following manner*:

---

* The concept of entropy was introduced by R. Clausius (1865). The word "entropy" consists of two words: *en* meaning the proposition "in" and *trope* meaning a transformation; the literal translation is "transformation to". What was meant is the tendency towards the transformation of energy to less and less valuable forms of energy—the dissipation of energy.

(a) in a spontaneous process

$$dS > \frac{\delta Q}{T}$$

(b) in an equilibrium process

$$dS = \frac{\delta Q}{T} \tag{3.9}$$

(c) in a nonspontaneous process

$$dS < \frac{\delta Q}{T}$$

The ratio of the amount of heat absorbed to the temperature is called the *reduced heat.* Therefore, according to Eq. (3.9*b*) an increment in the entropy of the system is equal to the reduced heat. On the other hand, one should understand and remember that the entropy is a property of the system and the change in entropy is independent of the path and is only governed (as described in detail in Sec. 1.1) by the initial and final states of the system. As an example, let us consider two states of an ideal gas at the same temperature; they are represented by two points on the isotherm in Fig. 3.8 and by two different entropies, S_1 and S_2. Figure 3.8 shows several possible paths for the transfer of the system from state I to state II. It is clear that, irrespective of the path, the change in entropy, $\Delta S = S_2 - S_1$, will be the same. We can also consider the spontaneous transfer from state I to state II. To do this, let us go back to Fig. 2.16*a* which was used for the discussion of the expansion of a gas at an external pressure equal to zero and, hence, with no work being done. In this case, the work $W = 0$, the heat $Q = 0$ and the change in internal energy $\Delta U = 0$, the increase in entropy remaining the same, i.e., ΔS. For an infinitesimal spontaneous change in the system the inequality (3.9*a*) will hold, i.e., the increment in entropy of the system in question (a gas) will be greater than the reduced heat, which is equal to zero in this particular example. In an equilibrium expansion of the gas by means of the method discussed in Sec. 2.9 (see Figs. 2.16 and 2.17) the system will do a maximum work and absorb a maximum amount of heat. According to Eq. (2.25),

$$W_T = Q_T = n\,RT \ln \frac{v_2}{v_1}$$

Using the equality $dS = \delta Q/T$ (3.9*b*) for an equilibrium process, we can write a finite change in entropy of the gas at constant temperature:

$$\Delta S = \frac{Q_T}{T} = nR \ln \frac{v_2}{v_1} \tag{3.10}$$

Here, (3.9*b*) has been integrated, with the constant temperature taken outside the integral sign. If the gas is compressed from state II to state I, then under equilibrium conditions the entropy of the gas will decrease by the same amount, ΔS, which can be calculated from Eq. (3.10). But when the gas is compressed at a finite rate, when the piston is loaded with weights of finite size (the upper step-like curve, Fig. 2.17), i.e., in a nonspontaneous process, inequality (3.9*c*) should be used. In other words, the absolute value of the work expended and of the heat evolved will in this case be greater than $W_T = Q_T$, i.e.,

$$|W_{\text{com}}| > W_T \text{ and } |Q_{\text{com}}| > Q_T \tag{3.11}$$

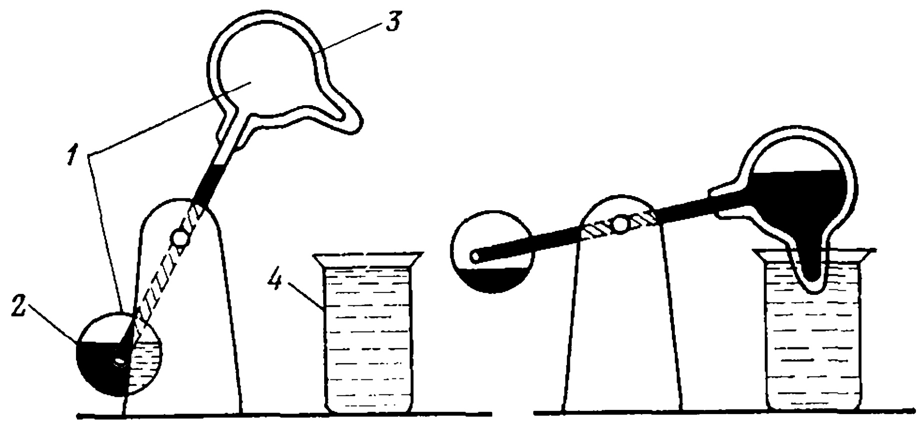
And since the change in entropy remains the same in absolute magnitude, it follows that

$$dS < \frac{\delta Q}{T} \quad \text{or} \quad \Delta S < \frac{Q_{\text{com}}}{T} \tag{3.12}$$

In discussing the second law in the form (3.9) one should bear in mind that ΔS is here the entropy change only for a particular closed system picked out for study from the universe. Thus, for example, this may be a vessel in which a chemical reaction occurs. The given system interacts with heat sources and other systems, doing work. It is essential that the change in entropies of these interlinked systems is not included in ΔS from Eqs. (3.9) and (3.12). But the total change in entropy is always positive.

The possibility cannot be excluded that the new property stipulated by the second law, i.e., the *entropy*, will seem at first glance somewhat abstract and obscure. However, the entropy concept is not, in essence, more difficult than the concept of *energy*, which is familiar to us from school days. On the contrary, the entropy concept is easier to understand than the energy concept. A quite spectacular idea about the entropy is furnished by its interpretation based on molecular-kinetic conceptions (see Chapter 6). At this point we are, first of all, to learn how to calculate the entropy change in various equilibrium processes and thereby to know what states have a lower and what a greater entropy.

In concluding this section concerned with the second law we shall consider, as an example of the possible use of energy ("heat") of the surroundings, the scheme of a Chinese toy known as the "drinking bird" (Fig. 3.9*a* and *b*). Once triggered to action, which is done by bringing it to position *b*, the "bird" continues to swing up and down: in one position it "drinks" water from the glass and then returns to the upper position, in a seemingly perpetual motion. A detailed analysis of the action of the toy shows, however, that it corresponds to the laws of thermodynamics. As seen from Fig. 3.9, the "bird" consists of two flasks joined by a tube, these flasks containing a volatile liquid and hermetically sealed. The entire system is capable of rotating about its axis fixed in the stationary support, the position of equilibrium shown on the left of the figure. The head of the "bird" is covered by a layer of a moisture-absorbing material, cotton wool. The system is brought into action by moistening the head, say, when the beak is dipped in water, as in position *b*. Then, the system acts on its own. Namely, water vaporizing from the coating of the head lowers its temperature by a few degrees as compared with the temperature of the body (and of the surroundings). This lowers the vapour pressure in the head chamber. The pressure difference that arises runs the liquid in the direction of the head. The centre of gravity is shifted, the head becomes heavier and bends forward. At the turning point of motion the "bird" assumes a nearly horizontal position, as shown on the right. The beak dips in water, maintaining the moisture content of the head coating. The end of the connecting tube emerges from the liquid residue in the left flask. In this position of the system the hydrostatic pressure of the liquid becomes less than the vapour pressure difference, as a result of which the vapour runs through the tube from left to right, balancing the pressure. Then, when the liquid being acted on by the force of gravity flows back into the left flask, the initial position of equilibrium is restored and the cycle then repeats itself. The "drinking bird" acts better at a higher temperature and a lower moisture content. With a relative moisture content close to 100 per cent the action discontinues. The working substance must have a high vapour pressure, a higher density and a low heat of vaporization; Freon-11 (CCl_3F) is a suitable substance. The efficiency of the system can be increased by replacing water in the beaker with a more volatile liquid.



(a) (b)

Fig. 3.9. The "drinking bird":
1—geometric flasks joined by a tube; 2—volatile liquid (freon CCl_3F); 3—water-soaking coating of the flask (cotton wool); 4—water (or a more volatile liquid).

The "drinking bird" undoubtedly does work and we leave it to the reader to prove that its operation does not contradict the first and second laws of thermodynamics.

3.3. The Integrating Factor for the Heat of an Equilibrium Process

In this section we shall consider an elementary route for introducing the entropy concept by way of proving the existence of an integrating factor for the heat of an equilibrium process. Heat is not, in essence, a property of a system but it becomes a property when multiplied by an integrating factor. In this connection, we can say that from a mathematical point of view the formulations of the first and second laws of thermodynamics are based on constructing exact differentials from infinitesimal quantities. For example, an infinitesimal amount of heat taken by a system is not an exact differential, just as the work done by the system, but their difference [see Eq.

(2.20)] $\delta Q - \delta W = dU$ is equal according to the postulate, to the exact differential of the internal energy of the system—an increment in its property U. A similar approach is also possible for the second law. Expressions of the type

$$\delta q = M(x, y)\,dx + N(x, y)\,dy \tag{3.13}$$

are called, in mathematics, the Pfaffian equations which may be and may not be exact differentials. In the first case Euler's rule of cross differentiation holds true:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

But if Eq. (3.13) is not an exact differential and is the sum of infinitesimal quantities, then the two-term expression (3.13) can always be converted into an exact differential by multiplying by the integrating factor $G(x, y)$.

In this case, $G(Mdx + Ndx)$ becomes an exact differential of a certain function of x and y. For example, the differential expression

$$ydx - xdy \tag{3.14}$$

turns into an exact differential through multiplication by $G(x, y) = \frac{1}{x^2}$ since

$$dF(x, y) = \frac{ydx - xdy}{x^2} = d\left(-\frac{y}{x}\right)$$

In this case, there are also other integrating factors, say, $1/y^2$, $1/xy$, $1/(x^2 + y^2)$, which convert (3.14), respectively, to $d(x/y)$, $d \ln (x/y)$, and $d\,|\arctan (x/y)|$. At a later time it will be proved that for the Pfaffian differential equation of two independent variables there always exists an integrating factor or, in other words, it is always *holonomic*.

Let us consider the Pfaffian differential expression for three and more variables; for example,

$$\delta q(x, y, z) = M(x, y, z)\,dx + N(x, y, z)\,dy + R(x, y, z)\,dz \tag{3.15}$$

Consider two possibilities: $\delta q(x, y, z)$ is an exact differential and δq is not. In the former case, there exists a function $F(x, y, z)$, whose exact differential is equal to δq, i.e.,

$$dF = \left(\frac{\partial F}{dx}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y} dz = \delta q(x, y, z) \tag{3.16}$$

Equating the coefficients in the differentials of the independent variables, (3.15) and (3.16), we see that

$$M(x, y, z) = \left(\frac{\partial F}{\partial x}\right)_{y,z}; \quad N(x, y, z) = \left(\frac{\partial F}{\partial y}\right)_{x,z};$$
$$R(x, y, z) = \left(\frac{\partial F}{\partial z}\right)_{x,y} \tag{3.17}$$

Further, by way of cross differentiation we find three relations for each pair of variables:

$$\frac{\partial M}{\partial y}=\frac{\partial N}{\partial x};\quad \frac{\partial N}{\partial z}=\frac{\partial R}{\partial y};\quad \frac{\partial R}{\partial x}=\frac{\partial M}{\partial z} \tag{3.18}$$

These reciprocity relations are necessary and sufficient for $\delta q\ (x, y, z)$ to be an exact differential. But if the conditions (3.18) are not fulfilled, then the Pfaffian three-term expression (3.15) is not an exact differential. Here again two cases are possible: for (3.15), just as for two variables, there exists an integrating factor, $G\ (x, y, z)$, which converts $\delta q\ (x, y, z)$ into an exact differential; in the second case, there may exist no integrating factor for a Pfaffian equation containing three or more variables. If there is an integrating factor, then the differential expression is called *holonomic* or *integrable*; otherwise, it is termed non-holonomic or non-integrable. If Eq. (3.15) is holonomic, there exists a function $G\ (x, y, z)$ such that

$$G\delta q = GMdx + GNdy + GRdz \tag{3.19}$$

is an exact differential and Euler's conditions lead to the following relations:

$$\frac{\partial GM}{\partial y}=\frac{\partial GN}{\partial x};\quad \frac{\partial GN}{\partial z}=\frac{\partial GR}{\partial y};\quad \frac{\partial GR}{\partial x}=\frac{\partial GM}{\partial z} \tag{3.20}$$

Differentiating these products and making certain algebraic transformations, we obtain the holonomicity condition for a Pfaffian expression containing three variables:

$$M\left(\frac{\partial R}{\partial y}-\frac{\partial N}{\partial z}\right)+N\left(\frac{\partial M}{\partial z}-\frac{\partial R}{\partial x}\right)+R\left(\frac{\partial N}{\partial x}-\frac{\partial M}{\partial y}\right)=0 \tag{3.21}$$

The case in question includes also a variant where δq is an exact differential at the very outset; only in this case is $G =$ const, for example, equals to unity. From the condition (3.21) it follows that the Pfaffian equation for two independent variables is unconditionally holonomic. Thus, if $\delta q = M\ (x, y)\ dx + N\ (x, y)\ dy$, then $R = 0$ and the coefficients M and N are independent of z. Hence, Euler's rule is fulfilled automatically.

We shall give here, without proof, the general case of the Pfaffian differential expression:

$$\delta q\,(x_1, x_2, \ldots, x_n)=\sum_{i=1}^{n} M_i\,(x_1, x_2, \ldots, x_n)\,dx_i$$

which is an exact differential if the reciprocity relation holds:

$$\frac{\partial M_i}{\partial x_j}=\frac{\partial M_j}{\partial x_i}\qquad (i, j=1, 2, \ldots, n)$$

for each of the $n\ (n - 1)/2$ pairs of variables. Or it is holonomic if the condition

$$M_i\left(\frac{\partial M_j}{\partial x_k} - \frac{\partial M_k}{\partial x_j}\right) + M_j\left(\frac{\partial M_i}{\partial x_k} - \frac{\partial M_k}{\partial x_i}\right) + \\ + M_k\left(\frac{\partial M_j}{\partial x_i} - \frac{\partial M_i}{\partial x_j}\right) = 0$$

holds for the various triplets of i, j, k.

Let us now turn to thermodynamics and write the first law in a general form for a closed system:

$$\delta Q = dU + \delta W \tag{3.22}$$

Further in the text (unless stated otherwise) we shall apply Eq. (3.22) to equilibrium processes and consider systems subjected to the action of the forces of external pressure only. Then, $\delta Q_{\text{eq}} = dU + p\,dv$. In dealing with a multicomponent system, in which a chemical reaction takes place, we can set $U = U\,(T, v, \xi)$ in accordance with Eq. (2.57) and write the first law in terms of the known coefficients (2.61):

$$\delta Q_{\text{eq}} = C_{v,\,\xi}\,dT + l_{T,\,\xi}\,dv + U_{T,\,v}\,d\xi \tag{3.23}$$

This is the Pfaffian differential equation for three independent variables. We shall first simplify the task by considering a closed one-component single-phase system with no chemical reactions taking place. In this case, $d\xi = 0$, $C_{v,\,\xi} = C_v$ and $l_{T,\,\xi} = l_T$ and Eq. (3.23) can be written in a simpler form:

$$\delta Q_{\text{eq}} = C_v\,dT + l_T\,dv = \left(\frac{\partial U}{\partial T}\right)_v dT + \left[p + \left(\frac{\partial U}{\partial v}\right)_T\right] dv \tag{3.24}$$

Thus, there is obtained a Pfaffian differential equation for two variables. According to what has been said about the mathematical properties of the Pfaffian equations, we assert that a Pfaffian equation is holonomic, i.e., it has an integrating factor, say, $g\,(T, v)$, which converts δQ_{eq} to an exact differential of a certain function $S\,(T, v)$:

$$dS = g\,(T, v)\,\delta Q_{\text{eq}} = g\,(T, v)\left\{\left(\frac{\partial U}{\partial T}\right)_v dT + \left[p + \left(\frac{\partial U}{\partial v}\right)_T\right] dv\right\} \tag{3.25}$$

Further establishment of the concrete form of the integrating factor $g\,(T, v)$ proves, however, to be impossible without additional physical information on the properties of the system, though the assertion itself of the existence of an integrating factor is doubtless.

The problem is easily solved for an ideal gas, an object which goes beyond the scope of thermodynamics. Thus, $p = nRT/v$, $(\partial U/\partial v)_T = 0$, and $(\partial U/\partial T)_v = C_v = dU/dT$, i.e., the heat capacity is a function of temperature only. With these data in view, the Pfaffian equation (3.24) transforms to

$$\delta Q_{\text{eq}} = C_v(T)\, dT + nRT \frac{dv}{v} \tag{3.26}$$

which when divided by T turns into an exact differential:

$$\frac{\delta Q_{\text{eq}}}{T} = C_v(T) \frac{dT}{T} + nR \frac{dv}{v} \tag{3.27}$$

which can be proved by performing a cross differentiation:

$$\left[\partial \left(\frac{C_v}{T}\right) \Big/ dv\right]_T = \left[\partial \left(\frac{nR}{v}\right) \Big/ \partial T\right]_v = 0$$

Thus, the integrating factor here is equal to the inverse temperature, $g(T, v) = 1/T$. We introduce the following notation:

$$dS = \frac{\delta Q_{\text{eq}}}{T} \tag{3.28}$$

and since dS is an exact differential, S is a property of the system called the *entropy*. The essence of the second law in this interpretation consists in that expression (3.28) is of general validity and applies not only to an ideal gas. However, the existence of an integrating factor for the heat defined by a Pfaffian differential equation containing three variables; for example,

$$\delta Q_{\text{eq}} = C_{x,\xi}\, dT + l_{T,\xi}\, dv + U_{T,v}\, d\xi$$

the more so with any number of variables, requires special proof. In the most general form, this proof is carried out on the basis of the above-mentioned principle of adiabatic unattainability (see Sec. 3.2) and the Carathéodory theorem.

On this path one deals with an adiabatic process for which the Pfaffian differential expression turns into a Pfaffian equation:

$$\delta Q_{\text{eq}} = \sum_{i=1}^{n} M_i(x_1, x_2, \ldots, x_n)\, dx_i = 0 \tag{3.29}$$

and then proves, with the aid of the Carathéodory theorem, that this equation has a solution and, hence, that the initial differential expression is holonomic and has the integrating factor $1/T$. A rigorous and correct proof of this proposition requires unwieldy mathematical computations that can be found in the specialized literature. Here we shall show that the same results can be obtained in an incomparably simpler way, with the aid of an ideal gas.

Let the state of the system under consideration to be defined by n variables and the expression of the first law have the following form:

$$\delta Q_{\text{eq}} = \sum_{i=1}^{n} M_i(x_1, x_2, \ldots, x_n)\, dx_i \tag{3.30}$$

We put an ideal-gas thermometer (Fig. 3.10) into this system and make the thus obtained complex system heat-insulated. By virtue of the adiabatic nature of any change in the system, heat exchange is possible only between the initial system A and the thermometer B. Therefore, for an infinitesimal change in the complex system

$$\delta Q + \delta Q_1 = 0 \tag{3.31}$$

if δQ is the heat received by the initial system and is defined by an expression of the type (3.30), and δQ_1 refers to an ideal gas (thermometer) and is expressed by relation (3.26), i.e.,

$$\delta Q_1 = C_v(T)\,dT + nRT\frac{dv}{v}$$

We divide Eq. (3.31) by the temperature of the entire system and obtain:

$$\frac{\delta Q}{T} + \frac{\delta Q_1}{T} = 0 \tag{3.32}$$

But for an ideal gas, according to (3.28), $\delta Q_1/T$ is equal to an exact differential which we shall denote as dS_1. Then, for the original arbitrary system

$$\frac{\delta Q}{T} = -\frac{\delta Q_1}{T} = -dS_1 \tag{3.33}$$

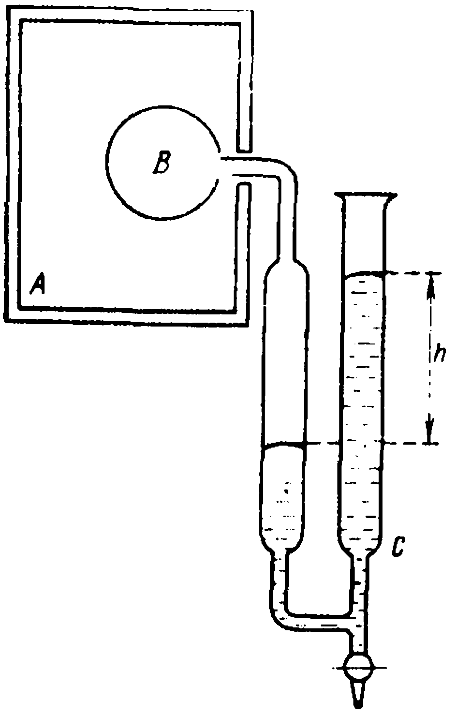


Fig. 3.10. A proof of the equality $\delta Q/T = dS$:

A—an arbitrary system; B—bulb of the (ideal) gas thermometer; C—mercury manometer of the thermometer.

In other words, the ratio $\delta Q/T$ for an arbitrary system and an arbitrary equilibrium process is equal to an exact differential which can be designated by $dS = -dS_1$. Thus, with the aid of an ideal gas we have proved the general significance of the relation

$$\frac{\delta Q_{\text{eq}}}{T} = dS$$

which defines the change in entropy of the system as its property and has the meaning of the first part of the second law. The second part consists in stating the inequality

$$dS > \frac{\delta Q}{T}$$

for spontaneous non-equilibrium processes.

3.4. Application of the Second Law to an Isolated System. Criteria of Equilibrium and Spontaneity

Of special interest is the application of the second law of thermodynamics in the form (3.9), i.e., of the law of entropy, to an isolated system. Generally speaking, an isolated system is a system placed under imaginable conditions that exclude the possibility of the exchange of material and any form of energy or work with other systems. We shall define the thermodynamic isolated system more specifically, assuming that the internal energy and volume of the system are kept constant, i.e., $U =$ conts, $v =$ const or $dU = 0$, $dv = 0$. No heat exchange takes place in such a system, i.e., $\delta Q = 0$. By virtue of this, relations (3.9) will assume the following form for an isolated system:

$$\begin{aligned} &\text{(a) for a spontaneous process } dS > 0; \\ &\text{(b) for an equilibrium process } dS = 0; \\ &\text{(c) for a nonspontaneous process } dS < 0. \end{aligned} \tag{3.34}$$

This notation is of the most general form. However, since the third case is the inversion of the first, one most frequently restricts oneself to the first two cases, i.e., (a) and (b). Of course, one should bear in mind that if a nonspontaneous process occurred in an isolated system, say the self-compression of the gas in some part of the vessel, then the entropy of the system would be decreased. But from the classical standpoint this is impossible since it requires an expenditure of external work, and from the standpoint of molecular statistics this is hardly probable (see Chapter 6). Therefore, for an isolated system the second law is usually written in a more compact form:

$$dS \geqslant 0 \tag{3.35}$$

The entropy of an isolated system either increases or remains constant.

This formulation contains propositions which are extremely important to what follows. First, it contains a criterion of spontaneity for processes occurring in an isolated system. Only those processes that are accompanied by an increase in entropy can proceed on their own in such a system, i.e., can occur spontaneously. Such are, for example, the following processes: the mixing of gases; the equilibration of the pressure of a gas; the transfer of heat from a hotter part of the system to a colder part; the combination of hydrogen and oxygen to give water, etc. While taking place in an isolated system, all these processes increase its entropy. Thus, the inequality

$$dS > 0 \tag{3.36}$$

expresses the *criterion of spontaneity* for a process occurring in an isolated system.

If a spontaneous process increases the entropy of an isolated system, then the cessation of all processes, i.e., the establishment of a stable equilibrium state, will occur when the entropy of the system attains a maximum value. Figure 3.11 presents, on an arbitrary scale, the curve of the entropy change versus possible changes in an isolated system. Thus, the criterion for a stable equilibrium in an isolated system is the entropy maximum. Mathematically, this maximum condition is expressed by the relations

$$dS = 0 \text{ and } d^2S < 0 \quad (3.37)$$

where d^2S is a second-order differential. Its negative value shows that only a decrease in entropy is conceivable (but impossible from the standpoint of classical thermodynamics) from the point of the maximum (Fig. 3.11). Relations (3.36) and (3.37) lie at the basis of the estimation of the spontaneity or nonspontaneity of any processes, including chemical reactions, and also form the basis of the theory of equilibrium.

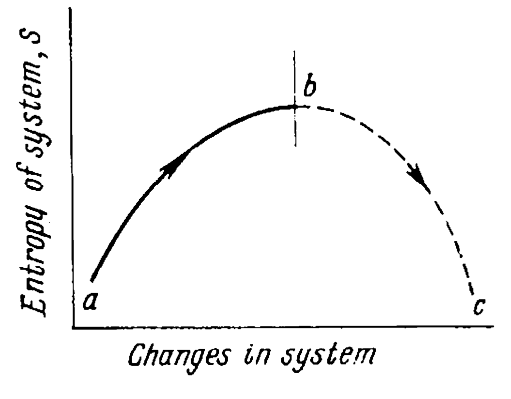


Fig. 3.11. The entropy change in an isolated system:

ab—entropy change in spontaneous processes; *bc*—entropy change in conceivable nonspontaneous processes; the point *b* corresponds to the equilibrium state of the system.

Let us consider the dimensionality of the entropy. From relations (3.9) it is seen that it coincides with the dimensions of heat capacity; the entropy can be expressed in the same units. Besides, the entropy is an extensive property and it is conveniently referred to the unit mass of a substance. The units of measurement of the entropy

$$S\left[\frac{\text{calorie}}{\text{deg}\cdot\text{mole}}\right] \quad (3.38)$$

are also called the *entropy units* (abbreviated to e.u.).

In connection with the above statement that the entropy is an extensive property, it is useful to return to the series (2.13), which expresses various kinds of work (energy) as the product of an intensive property by an increment in an extensive property. Referring to relation (3.9*b*), we write it in a form analogous to Eq. (2.13), i.e.,

$$\delta Q = T\,dS \quad (3.39)$$

In other words, the heat (of an equilibrium process) can be represented, by analogy with (2.13), as the product of an intensive property, e.g. temperature, by an increment in an extensive property, the entropy. Or, if the heat may be regarded as one of the forms of energy, then the entropy will represent an extensive property corresponding to this energy, just as, for example, the surface O in the changes in the internal energy, γdO.

3.5. The Entropy Change in Equilibrium Processes

In this section we shall be concerned with calculations of entropy changes in various equilibrium processes. These calculations will be based on relation (3.9*b*) which should be integrated for the final transformation from state I to state II:

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \tag{3.40}$$

where S_1 and S_2 are the entropies of the initial and final states, respectively.

Let us first consider the heating of bodies (substances). If it occurs at constant volume, then, according to Eqs. (2.26) and (2.31), the amount of heat required for the heating of a substance by dT will be given as follows:

$$\delta Q = nC_v\, dT \tag{3.41}$$

where n is the number of moles of the substance. Analogously, at constant pressure the amount of heat necessary for heating substances by dT will be expressed in terms of heat capacity at constant pressure:

$$\delta Q = nC_p\, dT \tag{3.42}$$

Substituting Eqs. (3.41) and (3.42) into Eq. (3.40), we find the changes in entropy of the substance attending the heating at constant volume:

$$\Delta S = n \int_{T_1}^{T_2} \frac{C_v dT}{T} \tag{3.43}$$

and at constant pressure:

$$\Delta S = n \int_{T_1}^{T_2} \frac{C_p dT}{T} \tag{3.44}$$

Strictly speaking, in order to evaluate the integrals of (3.43) and (3.44) it is necessary to know the dependence of heat capacity on temperature (see Chapter 2). However, sometimes if no high accuracy is required or the range of variation of temperature is narrow, the heat capacity may be considered to be independent of temperature, in which case relations (3.43) and (3.44) transform to the following approximate formulas:

$$\Delta S = nC_v \ln \frac{T_2}{T_1} \tag{3.45}$$

and

$$\Delta S = nC_p \ln \frac{T_2}{T_1} \tag{3.46}$$

When relations (3.43) and (3.44) are used for the region of low temperatures, the Debye functions (2.147) through (2.150) prove very useful; at higher temperatures, temperature power series of the types (2.127) and (2.131) find application. For instance, if we adopt for nitrogen the function (2.128), i.e.,

$$C_p = 6.5 + 0.001\ T \text{ cal/deg·mole}$$

then the change in entropy of one mole of gaseous nitrogen upon heating from the boiling temperature 77.32°K to the standard temperature 298.15K (25°C) is calculated from Eq. (3.44):

$$\Delta S = 6.5 \times 2.3 \log (298.15/77.32) + 0.001\ (298.15 - 77.32) =$$
$$= 8.775 + 0.221 = 8.996 \text{ cal/deg·mole (e.u.)}$$

Analysing formulas (3.43) through (3.46), one can arrive at the conclusion that *the heating of a body (a substance) invariably brings about an increase in its entropy.*

Let us now examine some isothermal processes. Various processes of the so-called phase transitions of the first kind (first-order phase transitions) occur at constant temperature: melting (fusion), evaporation (vaporization), sublimation, transformations of crystalline modifications. The equilibrium behaviour of such processes requires also that the pressure be kept constant. So, for constant temperature Eq. (3.40) leads to

$$\Delta S = \frac{1}{T} \int_1^2 \delta Q = \frac{Q_T}{T} \tag{3.47}$$

where Q_T is the heat of a finite isothermal process. If the pressure is also kept constant, then, according to Eqs. (2.94), (2.95) and (2.96), the heat will be expressed in terms of the enthalpy change:

$$Q_p = \Delta H$$

Therefore, the entropy change of substances attending a phase transition is written in the following general form:

$$\Delta S_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}} \tag{3.48}$$

Thus, for the phase transition H_2O (sld) → H_2O (liq) the heat (or enthalpy) of fusion $\Delta H_{\text{fus}} = 1436$ cal/mole. Thus, the fusion of one mole of ice at 0°C is accompanied by the following entropy change:

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} = \frac{1436}{273.15} = 5.256 \text{ e. u.} \tag{3.49}$$

that is, the entropy of one mole of liquid water is 5.256 entropy units greater than the entropy of ice. In general, one must understand and remember that since in phase transitions, such as melting (fusion), vaporization and sublimation, the heat is absorbed, i.e., $\Delta H > 0$, they are all associated with an increase in entropy. In connection with phase transitions it is useful to refer to an empirical principle known as *Trouton's rule*: *the entropy increase per mole during vaporization at the normal boiling temperature* ($p = 1$ atm) *is almost the same for various liquids and equals 21-22 entropy units.*

Table 3.1 gives some pertinent data; from these data it is seen that Trouton's rule is approximate. Very strong deviations from Trouton's rule are observed in the case of liquids that boil at very low temperatures (He and H_2) and also of associated liquids, such as water and ethyl alcohol. Trouton's rule can nevertheless be used to evaluate the heat of vaporization from known boiling temperature.

TABLE 3.1. **Trouton's Rule and Departures from It**

Substance	T_b, °K	ΔH_b, cal/mole	$\Delta S_b = \Delta H_b / T_b$, cal/deg·mole
Cl_2	239.5	4855	20.34
C_2H_6	184.1	3517	19.06
n-C_8H_{18}	398.7	8224	20.62
He	4.3	20	4.7
H_2	20	218	10.9
H_2O	373	9716	26
C_2H_5OH	352	9220	26.22

We shall now consider the entropy of an ideal gas, defining it as a function of temperature, volume and pressure and assuming equilibrium processes of the change of the state. Using Eqs. (2.21) and (3.9), we write the combined formula for the first and second laws:

$$T\,dS = dU + p\,dv \tag{3.50}$$

Here it is meant that the system is acted on only by the forces of external pressure. Instead of the differential of the internal energy, we substitute its expression from Eq. (2.30). The pressure is replaced with the aid of the equation of state for an ideal gas and all the terms are divided by T:

$$dS = nC_v \frac{dT}{T} + nR \frac{dv}{v} \tag{3.51}$$

We integrate Eq. (3.51), assuming the constancy of the heat capacity:

$$S_2 - S_1 = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1} \tag{3.52}$$

Here the entropy is simultaneously represented as a function of both temperature and volume. In particular, if $T_2 = T_1$, Eq. (3.52) changes to the earlier encountered relation (3.10):

$$\Delta S = nR \ln \frac{v_2}{v_1}$$

which defines the entropy change during the isothermal expansion of an ideal gas. In connection with the last formula it should be noted that an increase in the volume leads to an increase in the entropy of the gas: for example, if $n = 1$ and $v_2/v_1 = 10$, then

$$\Delta S = 1.987 \times 2.303 \log 10 \approx 4.576 \text{ cal/deg·mole}$$

When the temperature and volume are changed, the pressure of the gas can also change simultaneously. In order to find the dependence of the entropy on the pressure and volume, we express the ratio of the temperatures in terms of the ratio of the values of pv:

$$\frac{T_2}{T_1} = \frac{p_2 v_2}{p_1 v_1} \tag{3.53}$$

and substitute into Eq. (3.52). After simple rearrangements we obtain the following relation, taking cognizance of Eq. (2.40):

$$\Delta S = nC_v \ln \frac{p_2}{p_1} + nC_p \ln \frac{v_2}{v_1} \tag{3.54}$$

Finally, it is possible to replace the ratio of the volumes, taking advantage of the same relation, (3.53):

$$\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{p_1}{p_2} \tag{3.55}$$

At constant temperature Eq. (3.55) leads to a formula analogous to Eq. (3.10). It shows that as the pressure of the gas increases its entropy decreases. The relations derived here are used in calculations of the entropy change if the gas is reduced to standard conditions, and the conditions for the standard state of the gas imply its correspondence to the ideal gas equation.

For the reasons which will be clear at a later time (see Sec. 3.6), the determination of the entropy change for the equilibrium transition of a substance from the crystalline state at absolute zero (the entropy S_0) to the standard state at the temperature 298.15°K (the entropy S°_{298}) is very important. For example, H_2O (solid, 0°K) → → H_2O (vapour, 1 atm of ideal gas, 298°K). The equilibrium transition must involve several stages. The first stage is the heating of ice from 0°K to the boiling temperature. The entropy change is calculated from Eq. (3.44):

TABLE 3.2. **The Heat Capacity of Water at Low Temperatures, cal/deg·mole**

T, °K	C_p	$\frac{C_p}{T}$
10	0.03	0.003
30	1.05	0.035
100	3.84	0.0384
200	6.66	0.0333
260	9.21	0.0345
273.15	12.00	0.0439

$$S_{273,\,H_2O\,(sld)} - S_0 = \int_0^{273.15} C_p \frac{dT}{T} \tag{3.56}$$

As has already been said, the Debye function proves useful for the evaluation of the integral in such cases. But we shall make use of experimental values of heat capacity at different temperatures; some of these values are listed in Table 3.2.

Such data are used to plot a curve of C_p/T versus T (Fig. 3.12). This curve is extrapolated to 0°K and the area of the figure obtained, equal to the integral of (3.56), is measured in some way. It has been found that

$$\Delta S_1 = S_{273.15,\,H_2O\,(sld)} - S_0 = -9.9 \text{ cal/deg}\cdot\text{mole} \tag{3.57}$$

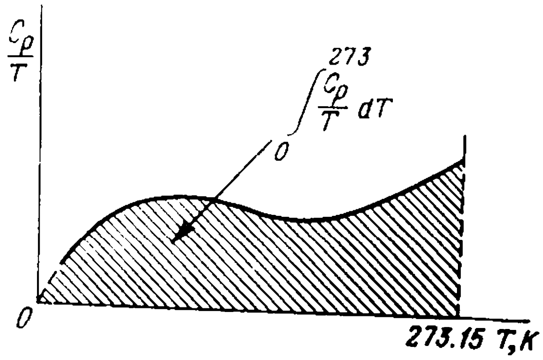


Fig. 3.12. Calculating the entropy change in ice upon heating from 0 to 273.15°K.

The second stage is a phase transition—water melts at 273.15°K. Here the calculation is carried out in accordance with Eq. (3.47); it has already been made in Eq. (3.49). Thus,

$$\Delta S_2 = S_{273,\,H_2O\,(liq)} - S_{273,\,H_2O\,(sld)} = 5.258 \text{ cal/deg}\cdot\text{mole} \tag{3.58}$$

At the third stage the liquid water is heated from the melting point up to 25°C (298.15°K). Here the temperature range is not wide and the heat capacity changes little and may be considered constant, using formula (3.45):

$$\Delta S_3 = S_{298,\ \mathrm{H_2O\,(liq)}} - S_{273,\ \mathrm{H_2O\,(liq)}} =$$
$$= 18.3 \times 2.303 \log \frac{298.15}{273.15} = 1.60 \text{ cal/deg·mole} \qquad (3.59)$$

At the next, fourth stage the water is to be subjected to equilibrium vaporization at a temperature of 25°C. The heat of vaporization at this temperature $\Delta H_{\mathrm{vapn}} = 10{,}514$ cal/mole. The saturated vapour pressure, i.e., the equilibrium pressure, is equal to 0.0313 atm—it is at this pressure that the vapour is produced. Thus,

$$\Delta S_4 = S_{298,\ \mathrm{H_2O\,(vap)},\ p=0.0313\ \mathrm{atm}} - S_{298,\ \mathrm{H_2O\,(liq)}} =$$
$$= 10{,}514/298.15 = 35.264 \text{ cal/deg·mole} \qquad (3.60)$$

Finally, at the fifth stage the vapour is subjected to an isothermal compression to the standard pressure equal to 1 atm. The behaviour of water vapour at a pressure of 0.0313 atm is close to that of an ideal gas; therefore, the entropy of the compression can be calculated from Eq. (3.55) putting $T_1 = T_2$:

$$S^{\circ}_{298,\ \mathrm{H_2O\,(vap)},\ 1\ \mathrm{atm}} - S_{298,\ \mathrm{H_2O\,(vap)},\ 0.0313\ \mathrm{atm}} =$$
$$= R\ 2.303 \log \frac{p_1}{p_2} = 1.987 \times 2.303 \log \frac{0.0313}{1} = -6.90 \text{ cal/deg·mole} \qquad (3.61)$$

The entropy at this stage decreases. Summing up the entropy changes at all the five stages, we find the ΔS value for the transition from absolute zero to the standard vapour state at 298.15°K:

$$S^{\circ}_{298,\ \mathrm{H_2O\,(vap)},\ 1\ \mathrm{atm}} - S_0 = 9.9 + 5.26 + 1.60 +$$
$$+ 35.264 - 6.90 = 45.12 \text{ cal/deg·mole} \qquad (3.62)$$

In this calculation the very occurrence of an entropy change at the fourth stage (vaporization) is worth attention. This observation is of sufficiently general importance and on its basis one can assert with certainty that the maximum entropy corresponds to the gaseous (vaporous) state of aggregation.

Let us examine one more process associated with the increase in entropy—the mixing of gases, which are considered here to be ideal and incapable of chemical interaction. Imagine a method of equilibrium isothermal mixing of two gases. Figure 3.13 shows a cylinder with two pistons, *1* and *2*, which contains two originally separated gases, A and B. The pistons are semi-permeable: the piston *1* is permeable to gas A and impermeable to gas B; the piston *2* is impermeable to gas A and permeable to gas B. The gas A freely passes through piston *1* and exerts a pressure on piston *2*. This pressure is equilibrated from outside by p_A. The pressure of the gas B exerted on piston *1* is also equilibrated from without by p_B. The entire system is immersed in a thermostat and therefore the temperature of the gases is maintained constant. If the external pressures are made lower by infinitesimal amounts than the pressures of the gases themselves, then each of them will expand independently of the other and will fill the entire volume of the cylinder, $v_1 + v_2$, and the gases will have been mixed. The equilibrium process can be reversed in direction. To do this, it is necessary that the external forces be greater than the pressures of the gases themselves. Each of the gases will be compressed isothermally until the pistons occupy the positions indicated in the figure and the gases are separated. Naturally, there will be expended work which is not difficult to calculate from the known formula for isothermal expansion or compression of the gas. Since the gases behave as though they were quite independent, the entropy change can be calculated for each of them separately from a relation of the type (3.10). Thus, for gas A

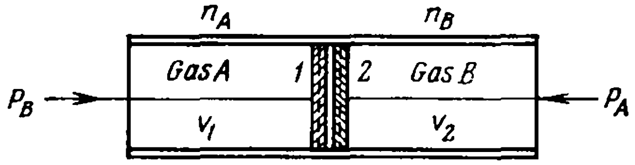


Fig. 3.13. Equilibrium mixing of gases.

$$\Delta S_A = n_A R \ln \frac{v_1 + v_2}{v_1} \tag{3.63}$$

and for gas B

$$\Delta S_B = n_B R \ln \frac{v_1 + v_2}{v_2} \tag{3.64}$$

The overall entropy change of the system upon mixing of the gases will be given by the following sum:

$$\Delta S = S_A + \Delta S_B = n_A R \ln \frac{v_1 + v_2}{v_1} + n_B R \ln \frac{v_1 + v_2}{v_2} \tag{3.65}$$

which is greater than zero. In other words, the entropy increases upon mixing of the gases. On spontaneous mixing of the gases, which occurs after the gases are allowed to mingle upon removal of the separating partition, the increase in entropy will be the same as that calculated for the equilibrium process—the entropy change is independent of the path of the process.* As an example, let us calculate the entropy change on mixing of equal amounts of gases occupying equal volumes, i.e., let us put $n_A = n_B = 1$ and $v_1 = v_2$. We thus obtain:

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* The entropy change of gases on mixing led to the famous Gibbs paradox. The above calculation of ΔS according to Eq. (3.65) does not single out the individual properties of gases. Therefore, it might seem that, however close the

$$\Delta S = 2R\,2.303 \log 2 = 2 \times 1.987 \times 2.303 \times 0.301 = \\ = 2.755 \text{ cal/deg·mole} \tag{3.66}$$

3.6. The Planck Postulate (the Third Law of Thermodynamics)

It may seem that all the formulas derived in the preceding section, including formula (3.65), can be used to determine only the change in entropy but not its absolute value. In this sense, the entropy evidently does not differ from the other thermodynamic functions—the internal energy and enthalpy. But this is not so, and the reason behind it, as will be shown at a later time, lies in the special features of the entropy which link it with the disorder of the molecular state of the system. So far we know that the lowest entropy is exhibited by a substance in the solid state at absolute zero—we have seen in the preceding section that all processes leading to the transition of a substance from this state to any other state involve an increase in entropy. In 1911 Planck advanced the postulate that at absolute zero the entropy is not only the lowest but is simply equal to zero. The Planck postulate is formulated as follows: *The entropy of a perfect crystal of a pure substance at absolute zero is equal to zero.*

It is essential here to point out that a substance must be pure and the crystal must be free from defects. The presence of impurities and defects in the crystal lattice increases the entropy. Planck's statement was based on the properties of substances at temperatures close to the absolute zero which were already known at the time. According to the experimental data obtained at a later time and the theory [the Debye function (2.147)], the heat capacity not only tends to zero at $T \to 0$ but decreases much more rapidly than does the temperature, namely in proportion to its cube; therefore the integrand function (3.43) or (3.44) tends to zero with decreasing temperature.

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properties of two gases which differ in some respects are, on their mixing the entropy would change by the same amount (3.65). At the same time, for absolutely identical gases no increase in entropy must evidently occur. This jump in the behaviour of the entropy upon continuous transition from gases, which are similar in their properties but nevertheless differ in some respects, to gases, which are absolutely identical, constitutes the Gibbs paradox. Many scientists, including Einstein and Planck, have expended much time and effort to solve this paradox. The most satisfactory solution is perhaps obtained on the basis of quantum theory and statistical mechanics. (See, for example, B. M. Kedrov, *Three Aspects of Atomistics*, Part I. *The Gibbs Paradox*, Nauka Publishers, Moscow, 1969, in Russian; Ya. M. Gel'fer, V. L. Lyuboshits, and M. I. Podgoretsky, *The Gibbs Paradox and the Identity of Particles in Quantum Mechanics*, Nauka Publishers, Moscow, 1975, in Russian.)

We know that at low temperatures many of the properties of a body, including heat capacity, volume, entropy, are no longer dependent on temperature. In the thermodynamics of chemical reactions there is a theorem known as *Nernst's heat theorem*, according to which the derivative of the heat effect with respect to temperature tends to zero with decreasing temperature. All this cannot, of course, serve as a proof of Planck's postulate. A more convincing explanation for Planck's postulate is furnished by statistical thermodynamics (see Chapter 6), according to which the entropy is a measure of the disorder of the molecular state of the system. From this standpoint, a crystal having a perfect crystal lattice at absolute zero is an example of the maximum order and its entropy is equal to zero. The greatest entropy is displayed by the most random, chaotic gaseous state.

If we adopt the Planck postulate, it will turn out that the procedure similar to that described in the preceding section, namely the determination of the entropy upon equilibrium transition from the crystalline state at absolute zero to the standard state [relations (3.56) through (3.62)], provides not the entropy difference but the absolute value of the entropy of a substance in the standard state. We know that S_0 in Eq. (3.62) and also in other formulas is equal to zero. Further in the text we shall speak of the *standard entropies* of substances: they are usually referred to the temperature 298.15°K, denoted as S°_{298} and are expressed in cal/deg·mole. Standard entropies are determined either by the above-described method on the basis of calorimetric data or by the methods of statistical thermodyna-

TABLE 3.3. The Standard Entropies of Selected Substances at 298.15°K, cal/deg·mole

Solid	S°_{298}	Liquid	S°_{298}
Ag	10.20	Br_2	36.4
AgCl	23.00	HNO_3	37.19
AgBr	25.60	H_2O	16.73
AgI	27.6	Hg	18.17
Al	6.77	Gases	
As	8.4	CH_4	44.47
C (graphite)	1.37	CO	47.30
Ca	9.95	CO_2	51.08
CaO	9.5	Cl_2	53.29
CdO	12.37	F_2	48.49
Cu	7.97	H_2	31.21
Fe	6.49	HCl	44.64
I_2	27.76	H_2S	49.13
S (rhombic)	7.62	N_2	45.77
Si	4.51	NO	50.34
SiO_2 (quartz-ß)	10.00	O_2	49.01

mics for ideal gases which make use of the molecular characteristics. These latter methods are described in Chapter 6.

Table 3.3 presents the standard entropies of some selected substances; it should be noted that standard entropies play an important role in chemistry, namely in calculations of chemical equilibrium and in the determination of the criteria of the possible spontaneous occurrence of a reaction.

The Planck postulate is often called the third law of thermodynamics. While not denying the importance of this postulate and not disputing the latter term, we shall nevertheless remark that the theoretical and practical importance of the Planck postulate is much less than that of the first and second laws of thermodynamics.

Chapter 4

Application of the Second Law of Thermodynamics to Isothermal Systems

4.1. Criteria of Spontaneity and Equilibria. Helmholtz and Gibbs Free Energy

The second law of thermodynamics in the form

$$dS \geqslant 0$$

provides criteria of spontaneity for processes taking place in an isolated system ($dS > 0$) and criteria of equilibrium in such a system, to which there corresponds the maximum value of entropy or $dS = 0$ and $d^2S < 0$. Proceeding from these criteria, one could have built the entire theory of equilibrium for physico-chemical systems. In Chapter 5 it will be shown how formula (3.35) can be used to obtain, for example, the law of mass action, one of the important laws in chemistry. This route is, however, complicated and inconvenient, since it is too cumbersome—the entire system must be isolated, and if a chemical reaction is conducted at constant temperature, a thermostat must be placed within the system.

In practice, another route is used, the one suggested by J. Gibbs. This route consists in applying the second law of thermodynamics to non-isolated systems in which a constant temperature is maintained. Furthermore, it is assumed that the volume or pressure is also kept constant in the system. On the whole, the conditions imposed on the system correspond to conditions under which the heat effects of chemical reactions are determined (Chapter 2).

We shall begin with the constancy of temperature and volume, i.e., $T = \text{const}$ and $v = \text{const}$.

In order to obtain the required results, we shall first write down the combined formula for the first and second laws of thermodynamics on the basis of (2.20) and (3.9*a* and *b*):

$$T\,dS \geqslant dU + \delta W \text{ (a closed system)} \qquad (4.1)$$

We shall, however, assume that the system in question is subject to the action of only the forces of external pressure; combining the first and second laws, we have:

$$T\,dS \geqslant dU + p\,dv$$

or

$$dU - T\,dS + p\,dv \leqslant 0 \tag{4.2}$$

Now let the volume and temperature be constant; then $p\,dv = 0$ and relation (4.2) can be written as follows:

$$d\,(U - TS)_{T,v} \leqslant 0 \tag{4.3}$$

where the equality sign refers to equilibrium processes and the "lower than" sign to spontaneous non-equilibrium processes. For further discussion we shall designate the combination of the functions—the properties of the system—by a single letter, using the relation

$$F \equiv U - TS \tag{4.4}$$

to define a new extensive property of the system which has the dimensions of energy. This thermodynamic function was originally introduced by Massieu (1869) and later by Gibbs (1875), but it became widely known in Europe after the publication of an article by Helmholtz (1882). It is for this reason that the function F is called (perhaps, unjustly) the *Helmholtz free energy** (this important quantity is also called the *work content*, the *Helmholtz energy*, and the *Helmholtz function*).

In terms of this new function relation (4.3) can be rewritten as

$$dF_{T,v} \leqslant 0 \tag{4.5}$$

First, this relation implies the criterion of spontaneity for processes occurring in systems in which the temperature and volume are kept constant. It is precisely in such systems that processes accompanied by a decrease in the Helmholtz free energy of the system occur spontaneously:

$$dF_{T,v} < 0 \tag{4.6}$$

or for a finite change $\Delta F_{T,v} < 0$.

Second, relation (4.5) contains also a criterion of equilibrium. Since any spontaneous process brings the system to a state of equilibrium and is simultaneously accompanied by a decrease in F, all spontaneous processes will stop, i.e., a stable state of equilibrium will be established, at the minimum value of F. Mathematically, this condition of stable equilibrium can be written thus:

$$dF = 0, \quad d^2F > 0 \tag{4.7}$$

If the Helmholtz free energy of the system is laid off along the ordinate on an arbitrary scale and the change of the system along the abscissa, this change being expressed, for example, by the chemical variable ξ, then the possible and conceivable changes in F will be expressed by the curve shown in Fig. 4.1.

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* In their book Lewis and Randall speak of the function A, implying $U - TS$ (or, more exactly, $E - TS$). Here E and U stand for the internal energy.

As has already been said above, the property of the system denoted by F is known as the Helmholtz free energy of the system. The answer to the question why it is called the free energy allows us to get a deeper insight into the physical significance of this important function. We shall write the combined formula for the first and second laws in the most general form:

$$T\,dS \geqslant dU + \delta W \tag{4.8}$$

which implies the performance, by the system, of any work δW and not only of the mechanical work of expansion, as was implied by (4.2). We solve relation (4.8) for the work element:

$$\delta W \leqslant T\,dS - dU$$

or

$$\delta W \leqslant -(dU - T\,dS) \tag{4.9}$$

If the temperature of the system is again kept constant, then, according to relations (4.3) and (4.4), we get:

$$\delta W_T \leqslant -dF \tag{4.10}$$

But if we imagine a finite isothermal transformation of the system, i.e., its transition from state I (U_1, S_1, F_1, . . .) to state II (U_2, S_2, F_2, . . .), then relation (4.10) can be written in the form of finite differences:

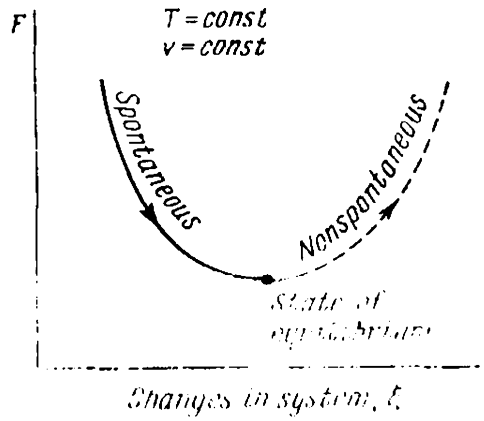

Fig. 4.1. Conceivable changes in the Helmholtz free energy (F) in a system in which the temperature and volume remain constant (to the state of equilibrium there corresponds a minimum of $F \equiv U - TS$).

$$W_T \leqslant F_1 - F_2 \text{ or } W_T \leqslant -\Delta F \tag{4.11}$$

It thus becomes clear that the work done by the system during an isothermal process is equal to or less than the loss in F, i.e., the Helmholtz free energy of the system undergoing a change. The equality holds for an equilibrium process in which the work being done by the system is at maximum. Hence,

$$W_{T\,(\max)} = F_1 - F_2 = -\Delta F \tag{4.12}$$

In other words, $-\Delta F$ of the system may be regarded as its ability to do work during an isothermal change. In an equilibrium isothermal process this possibility of work being done is completely realized [relation (4.12)]. But if the process occurs at a finite rate, i.e., if it is not at equilibrium, then, as a result of the inevitable losses, the amount of work will be less than the possible $W_{T\,(\max)}$, i.e., $W_T < -\Delta F$. Here we should again emphasize that ΔF will depend only on the initial and final states of the system, and the work W_T will be dependent also on the path followed during the transition of the system from the initial to the final state. For example, the explosion of oxyhydrogen gas ($2H_2 + O_2$) carried out in a calorimeter bomb (v = const) will be accompanied by a considerable decrease in F (the extent of the decrease will be calculated later), but no work will be done. On the other hand, the equilibrium occurrence of the reaction of formation of water in a hydrogen galvanic cell will make it possible, in principle, to convert the overall decrease in F into work.

Thus, regarding ΔF as the ability of the system to do work, we write $\Delta F = F_2 - F_1 = (U_2 - TS_2) - (U_1 - TS_1)$ or $\Delta F_T = \Delta U_T - T\Delta S_T$. The latter relation can be rewritten as

$$\Delta U_T = \Delta F_T + T\Delta S_T \tag{4.13}$$

From this relation it is seen that the change in the total (internal) energy of the system, i.e., ΔU_T, can be represented in the case of isothermal processes by two terms: the change in the Helmholtz free energy ΔF_T, which is equal to the possible maximum work $W_{T\,(\max)}$ [relation (4.12)], and the change in the bound energy $T\Delta S_T$. According to the basic formulation of the second law (3.9), the latter term is equal to the heat Q_{eq} evolved or absorbed by the system in an equilibrium process.

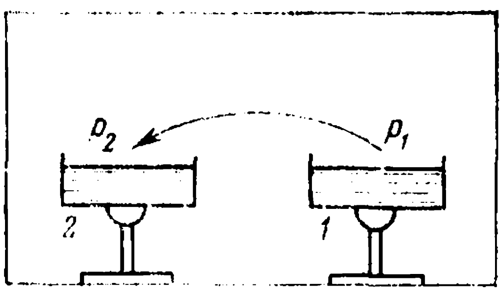

Fig. 4.2. The spontaneous transfer of water from vessel *1* (pure water) to vessel *2* (a solution of a nonvolatile substance) is accompanied by a decrease in the Helmholtz free energy: Calculated per mole: $\Delta F_{T,v} = -RT \ln \frac{p_1}{p_2} < 0$.

Let us consider, as an example, a process which occurs spontaneously at constant temperature and volume. Suppose we have a box containing two vessels (Fig. 4.2). The first vessel contains, say, pure water, and the second a solution of a nonvolatile substance, say, sodium chloride (common salt). As we know, the saturated vapour pressure above a pure solvent, p_1, is greater than the equilibrium vapour pressure p_2 above the solution (see Chapter 7). Therefore, a spontaneous process will take place in the box, namely, the transfer of water from the first to the second vessel. With the temperature being kept constant (and the constancy of the total volume is guaranteed by the constant dimensions of the box) the process must be accompanied by a decrease in the Helmholtz free energy of the system. Let us determine this decrease per mole of water. To do this, one should visualize, in accordance with Eq. (4.12), the equilibrium transfer of water from the first to the second vessel.

First, the water should be subjected to equilibrium evaporation at pressure p_1 and constant temperature. Suppose that the vessel with water is placed in a cylinder with a piston, as shown, for example, in Fig. 2.16*b*. The entire system must be placed in a thermostat (T = const). If the weight on the piston is less only by an infinitesimal amount than the force caused by the pressure p_1, the system will expand. The pressure will be kept constant and equal to p_1 due to the water being evaporated. The system will do the following work per mole of evaporated water:

$$W_{T(1)} = p_1 (\underline{v}_{\text{vap}} - \underline{v}_{\text{liq}}) \approx p_1 \underline{v}_{\text{vap}} \approx RT \tag{4.14}$$

In this calculation we neglected the small volume of the liquid as compared with the volume of the vapour and assumed that the product $p_1 \underline{v}_{\text{vap}}$ can be calculated by the ideal-gas law (see the footnote on page 135).

At the second stage of the equilibrium process the vapour pressure must be lowered isothermally (the vapour must be expanded) from pressure p_1 to pressure p_2. In this case, maximum work can be done:

$$W_{T(2)} = RT \ln \frac{p_1}{p_2} \tag{4.15}$$

Finally, the third stage is also conducted in the cylinder with a piston and a solution but this time the external pressure on the piston must be greater by an infinitesimal amount than the equilibrium vapour pressure p_2. The vapour is condensed into the solution and the work expended is

$$W_{T(3)} = p_2 (\underline{v}_{\text{liq}} - \underline{v}_{\text{vap}}) \approx -p\underline{v}_{\text{vap}} \approx -RT \tag{4.16}$$

The work at the first and third stages is mutually compensated and the net work of the equilibrium transfer of one mole of water from the vessel containing the solvent to the vessel with the solution is determined by the second stage, i.e., by relation (4.15). From this relation it is clear that, since $p_1 > p_2$,

$$W_{T(2)} > 0 \text{ and } \Delta F < 0 \tag{4.17}$$

and the process is accompanied by a decrease in the Helmholtz free energy. Knowing the pressure at the specified temperature, one can make a numerical calculation using Eq. (4.15).

Thus, the function F is convenient for the study of systems existing at constant temperature and volume. For chemists, however, the constancy of both temperature and pressure is more important since exactly these conditions are observed by the chemist when, for example, he boils water in an open beaker. These conditions are also observed (though only approximately) in industrial columns during the synthesis of ammonia or methanol. Thus, we shall deal with the criteria of spontaneity and equilibrium at constant temperature and pressure. We shall again proceed from Eq. (4.2), i.e., the combined formula for the first and second laws:

$$dU - T\,dS + p\,dv \leqslant 0 \tag{4.18}$$

Applying this formula to the conditions indicated above (T = const, p = const), we can take the differential sign outside the parenthesis:

$$d\,(U - TS + pv)_{T,\,p} \leqslant 0 \tag{4.19}$$

Then, we shall introduce the notation:

$$G \equiv U - TS + pv \equiv F + pv \equiv H - TS \tag{4.20}$$

which defines a new function denoted by G, which is an extensive property of the system and also has the dimensions of energy. It was introduced into thermodynamics by J. W. Gibbs (1875) and is called the *Gibbs free energy*. This quantity is also known as the *free energy* (this term without any name prefixed is frequently used), the *Gibbs energy*, the *Gibbs function* and the *Gibbs free-energy function*.

Thus, on the basis of relations (4.19) and (4.20) we come to the following expression for systems existing at constant temperature and pressure:

$$dG_{T,\,p} \leqslant 0 \tag{4.21}$$

In this expression the inequality holds for spontaneous processes and provides a criterion of spontaneity—the decrease in the Gibbs free energy:

$$dG_{T,\,p} < 0 \tag{4.22}$$

or for finite spontaneous changes of the system:

$$\Delta G_{T,\,p} < 0 \tag{4.23}$$

Since any spontaneous change of an isothermal system at constant pressure is associated with a decrease in G, a state of stable equilibrium is attained, i.e., to the cessation of all the processes there corresponds a minimum value of the Gibbs free energy, i.e., $dG = 0$, $d^2G > 0$. Using once more an arbitrary scale, we can depict possible and conceivable changes in G in the system with the aid of a graph (Fig. 4.3). To ascertain the physical meaning of the Gibbs free energy, we write the combined formula for the first and second laws in a general form for a closed system:

$$dU - T\,dS + \delta W \leqslant 0 \tag{4.24}$$

Here it is assumed that the system may be acted on by various forces, for example, electrical forces, and, hence, various kinds of work other than the mechanical work of expansion (pressure-volume work) may be done. In this connection, the total work δW can be divided into two parts—the mechanical work (pressure-volume work) associated with the change in volume, $p\,dv$, and the rest of the work, δW_{useful}, which we shall call the useful work. Thus,

$$\delta W = \delta W_{\text{useful}} + p\,dv$$

in which case relation (4.24) becomes:

$$\delta W_{\text{useful}} \leqslant -(dU - T\,dS + p\,dv) \tag{4.25}$$

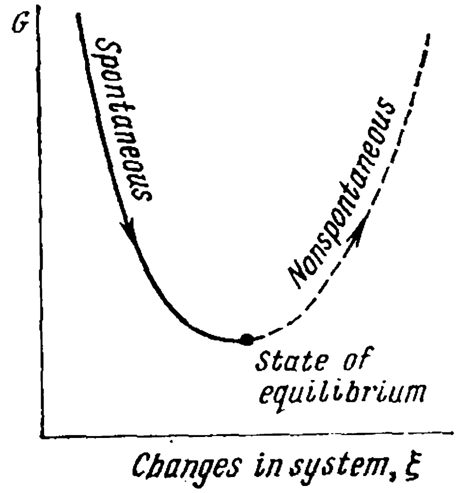

Fig. 4.3. Conceivable changes in the Gibbs free energy (G) in a system in which the temperature and pressure remain constant. (To the state of equilibrium there corresponds a minimum of $G \equiv H - TS$).

We shall again introduce restraints imposed by constant temperature and pressure and take the differential outside the parenthesis:

$$W_{\text{useful}} \leqslant -dG_{T,p} \tag{4.26}$$

or, for finite changes of the system:

$$W_{\text{useful}} \leqslant -\Delta G_{T,p} \tag{4.27}$$

The equality holds for equilibrium processes when the work being done by the system is at a maximum. Thus,

$$(W_{\text{useful}})_{\max} = -\Delta G_{T,p} \tag{4.28}$$

where $-\Delta G_{T,p}$ is a measure of the maximum useful work that can be done by the system during an equilibrium process at constant temperature and pressure. It is natural that the work done in a spontaneous nonequilibrium process will be less ($W_{\text{useful}} < -\Delta G$). Thus, $-\Delta F_T$ is a measure of the total possible work in

TABLE 4.1. **Criteria of Spontaneity of Processes and of Equilibrium for Certain Conditions of Existence of the System**

Conditions for existence of the system	Criterion of spontaneity	Criterion of equilibrium
An isolated system ($U =$ const, $v =$ const)	An increase in entropy $dS > 0$	Entropy maximum $dS = 0$, $d^2S < 0$
An isothermal system at constant volume ($T =$ const, $v =$ const)	A decrease in Helmholtz free energy $dF < 0$	A minimum of Helmholtz free energy $dF = 0$, $d^2F > 0$
An isothermal system at constant pressure ($T =$ const, $p =$ const)	A decrease in Gibbs free energy $dG < 0$	A minimum of Gibbs free energy $dG = 0$, $d^2G > 0$

any isothermal process, including those taking place at constant pressure, and $-\Delta G_{T,\,p}$ is a measure of the possible useful work.

Table 4.1 presents criteria of spontaneity of processes and also of equilibrium for various conditions under which the system may exist. This table could be extended with the entropy constancy being included in the conditions of existence of the system, but for practical purposes this is not required. It is up to the reader to formulate criteria for the constancy of volume and entropy and also for constant pressure and entropy.

4.2. Characteristic Functions

We have already been acquainted with the following thermodynamic functions—the properties of a system: the internal energy U; the enthalpy H; the entropy S; the Helmholtz free energy F; the Gibbs free energy G. Each of these properties may be represented as a function of various variables defining the state of the system. However, in systems consisting of individual substances, two variables natural for this or that function can be assigned to each of them. In this case, a function becomes *characteristic and the various properties of the system are explicitly expressed in terms of its derivatives of various orders*. For example, the internal energy is a characteristic function of the variables volume and entropy, i.e.,

$$U = f(v,\ S) \tag{4.29}$$

If we write the combined formula for the first and second laws for systems subject to the action of only the forces of pressure for an equilibrium process [relations (2.21) and (3.9*b*)]:

$$T\,dS = dU + p\,dv \tag{4.30}$$

and solve this relation for dU, we shall obtain

$$dU = T\,dS - p\,dv \tag{4.31}$$

Now, assuming either the entropy or the volume to be constant, we can write the following partial derivatives:

$$\left(\frac{\partial U}{\partial S}\right)_v = T \quad \text{and} \quad \left(\frac{\partial U}{\partial v}\right)_S = -p \tag{4.32}$$

Thus, the derivative of the internal energy with respect to the entropy at constant volume is equal to the temperature, and the derivative of U with respect to volume at constant entropy is equal to the negative pressure. With other variables one cannot obtain such a simple expression for the properties of the system in terms of the derivatives of the internal energy. Hence, for the internal energy the volume and entropy are natural variables of which it is a characteristic function. If the derivatives of (4.32) are differentiated once again, but each with respect to another variable, the mixed second derivatives will be obtained:

$$\frac{\partial^2 U}{\partial S\,\partial v} = \left(\frac{\partial T}{\partial v}\right)_S \tag{4.33}$$

and

$$\frac{\partial^2 U}{\partial v\,\partial S} = -\left(\frac{\partial p}{\partial S}\right)_v \tag{4.34}$$

The value of the mixed derivatives of continuous functions is independent of the order of differentiation, and therefore, on the basis of (4.33) and (4.34), we can write the following equality:

$$\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_v \tag{4.35}$$

As known, the equality holds if the derivatives are inverted; in other words, if the derivative of the volume is taken with respect to temperature and that of entropy with respect to pressure, i.e.,

$$\left(\frac{\partial S}{\partial p}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_S \tag{4.36}$$

The relation obtained is one of the so-called *Maxwell equations.* We shall call it the first Maxwell equation.

Let us now consider the enthalpy. According to the definition (2.78),

$$H \equiv U + pv$$

If the quantity H is differentiated, i.e., if we write

$$dH = dU + p\,dv + v\,dp \tag{4.37}$$

and dU in (4.37) is replaced with the aid of (4.31), the following expression is obtained for the differential of the enthalpy:

$$dH = T\,dS + v\,dp \tag{4.38}$$

On the basis of Eq. (4.38) we can write two partial derivatives:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \tag{4.39}$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = v \tag{4.40}$$

which show that the enthalpy is a characteristic function of the variables: entropy and pressure. Equating the second mixed derivatives gives, after inversion, the second Maxwell equation:

$$\left(\frac{\partial S}{\partial v}\right)_p = \left(\frac{\partial p}{\partial T}\right)_S \tag{4.41}$$

Recall now the definition of the Helmholtz free energy:

$$F \equiv U - TS$$

Differentiating and again replacing dU in (4.30), we obtain the differential

$$dF = -S\,dT - p\,dv \tag{4.42}$$

which enables us to write, first, the derivatives

$$\left(\frac{\partial F}{\partial T}\right)_v = -S \tag{4.43}$$

and

$$\left(\frac{\partial F}{\partial v}\right)_T = -p \tag{4.44}$$

and, second, the third Maxwell equation

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{4.45}$$

Here the natural variables are the volume and temperature, i.e., the properties of the system which are accessible to direct measurement.

Let us now show that the Gibbs free energy is a characteristic function of temperature and pressure. According to the definition (4.20),

$$G \equiv U - TS + p\,dv$$

Hence, taking cognizance of Eq. (4.30), we get

$$dG = -S\,dT + v\,dp$$

and

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{4.46}$$

and also

$$\left(\frac{\partial G}{\partial p}\right)_T = v \tag{4.47}$$

These derivatives are perhaps of greatest importance among those considered in this section; they will be resorted to repeatedly in the text.

From the derivatives (4.46) and (4.47) we can derive, by means of the methods already known, the fourth Maxwell equation:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \tag{4.48}$$

Note that all the four Maxwell equations have something in common: on the one hand, they are the derivatives of the entropy with respect either to the pressure (such a derivative is negative) or to the volume, and on the other hand, they are the derivatives of either the volume or the pressure, respectively, with respect to temperature. The Maxwell equations, especially the last two equations, find various applications in physical chemistry. For instance, they are used to write thermodynamic equations of state. If Eq. (4.30) is divided by the differential of the volume and the temperature is assumed to be constant, we shall have:

$$T\left(\frac{\partial S}{\partial v}\right)_T=\left(\frac{\partial U}{\partial v}\right)_T+p \tag{4.49}$$

Replacing now $(\partial S/\partial v)_T$ in the third Maxwell equation, we obtain one of the thermodynamic equations of state:

$$p=T\left(\frac{\partial p}{\partial T}\right)_v-\left(\frac{\partial U}{\partial v}\right)_T \tag{4.50}$$

The second thermodynamic equation of state is found by proceeding from the differential of the enthalpy (4.38). Dividing dH by dp and assuming the temperature constant, we arrive at the equation

$$\left(\frac{\partial H}{\partial p}\right)_T=T\left(\frac{\partial S}{\partial p}\right)_T+v \tag{4.51}$$

We solve it for the volume and replace $\partial S/\partial p$ in the fourth Maxwell equation:

$$v=T\left(\frac{\partial v}{\partial T}\right)_p+\left(\frac{\partial H}{\partial p}\right)_T \tag{4.52}$$

Equations (4.50) and (4.52) express, in differential form, the dependence of the pressure and volume on the other properties of a substance, in particular a gaseous substance. Any empirical equation of state must satisfy these general equations. They play an important role in thermometry, providing a theoretical basis for gas thermometers. For real gases, such as hydrogen or air, the volume at constant pressure is not strictly proportional to temperature. If the values of $\partial H/\partial p$ are determined (by measuring the Joule-Thompson effect), then it becomes possible to introduce requisite corrections, i.e., corrections for the readings of gas thermometers.

Let us apply the first of the thermodynamic equations of state, (4.50), to an ideal gas, for which

$$p=\frac{RT}{v}$$

Differentiating p with respect to temperature at constant volume and substituting the result into (4.50), we obtain the following relation:

$$\left(\frac{\partial U}{\partial v}\right)_T=0 \tag{4.53}$$

which implies that the internal energy of the ideal gas is independent of the volume (and pressure) at constant temperature. This proposition adopted here on the basis of the Gay-Lussac and Joule experiments is contained in the state equation of an ideal gas, which becomes clear now with the aid of the second law of thermodynamics. For real systems, $(\partial U/\partial v)_T$ is not, of course, equal to zero and is, as it were, a constituent part of the total overall pressure. According to Eq. (4.50), the pressure can be represented as the difference of two terms: the kinetic pressure

$$p_{\text{kin}} = T\left(\frac{\partial p}{\partial T}\right)_v \tag{4.54}$$

and the static or internal pressure

$$p_{\text{stat}} = \left(\frac{\partial U}{\partial v}\right)_T \tag{4.55}$$

The kinetic pressure results from the motion of molecules and is always positive. The static pressure results from the interaction of molecules: their attraction or repulsion. It may be either positive or negative. For example, hydrogen under ordinary conditions usually exerts a negative static pressure. The static pressure of carbon dioxide is positive. For example, at an external pressure of $p = 1$ atm and 290 °K, $(\partial U/\partial v)_T = 0.021$ atm. The kinetic pressure can be related with the thermal coefficients. Namely, with the volume thermal expansion coefficient (or volume expansivity):

$$\alpha = \frac{1}{v_0'}\left(\frac{\partial v}{\partial T}\right)_p \tag{4.56}$$

and with the isothermal compressibility:

$$\beta = -\frac{1}{v_0''}\left(\frac{\partial v}{\partial p}\right)_T \tag{4.57}$$

These two quantities are measured in physical experiments and their values are given in handbooks. To establish the relationship between p_{kin}, on the one hand, and α, β, on the other, we represent the pressure as a function of volume and temperature:

$$p = f(v, T) \tag{4.58}$$

Further, we take the total differential of p:

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT \tag{4.59}$$

Then, assuming the pressure to be constant ($dp = 0$), we divide Eq. (4.59) by dT:

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial p}{\partial T}\right)_v = 0 \tag{4.60}$$

Solving now Eq. (4.60) for $\partial p/\partial T$ and inverting the derivative $\partial p/\partial v$, we have

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T} = \frac{\alpha}{\beta} \tag{4.61}$$

Thus, using Eq. (4.61), we obtain the following expression for the kinetic pressure*:

$$p_{\text{kin}} = T\left(\frac{\partial p}{\partial T}\right)_v = T\frac{\alpha}{\beta} \tag{4.62}$$

Let us cite an example. At a temperature of 0°C and an external pressure equal to 250 atm the following values of the coefficients

TABLE 4.2. **The Kinetic Pressure of Selected Liquids**

Liquid	External pressure, atm	t, °C	$\alpha \cdot 10^4$, deg^{-1}	$\beta \cdot 10^6$, atm^{-1}	p_{kin}, atm
Hg	250	0	1.8197	3.65	13,600
		40	1.8079	3.83	14,800
		80	1.7993	4.02	15,800
		120	1.7936	4.22	16,700
		160	1.7921	4.42	17,600
		200	1.7944	4.65	18,300
CS_2	1	—80	10.57	47.3	4,317
		—40	11.04	62.0	4,150
		0	11.55	81.3	3,881
		40	12.11	106.5	3,558
CCl_4	26	20	11.83	100.9	3,438
		60	13.12	135.3	3,229
		100	14.46	198.3	2,720
		140	16.56	332.2	2,060
		180	21.93	544.1	1,826

have been found for mercury: $\alpha = 1.8197 \times 10^{-4}$ deg^{-1} and $\beta = 3.65 \times 10^{-6}$ atm^{-1}. Hence, under these conditions

$$p_{\text{kin}} = T\left(\frac{\partial p}{\partial T}\right)_v = 273.15\,\frac{1.82 \times 10^{-4}\ \text{deg}^{-1}}{3.65 \times 10^{-6}\ \text{atm}^{-1}} = 13{,}600\ \text{atm}$$

The static (or internal) pressure will be less by 250 atm, and this difference is balanced by the external pressure. Table 4.2 presents the values of the kinetic pressure for some selected liquids. As seen from this table, the pressure p_{kin} may either increase or decrease with increasing temperature; its decrease is probably associated with an increase in the volume of the liquid.

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* Strictly speaking, the volumes v_0' and v_0'' in (4.56) and (4.57) are not identical. In condensed systems, however, they are close to each other and their ratio may be assumed to be equal to unity.

Applying the third Maxwell relation, (4.45), to phase transitions (phase equilibria), we can deduce the Clausius-Clapeyron equation. In an equilibrium isothermal phase transition, say, liquid $\rightleftarrows$ vapour, the entropy change referred to unit volume change attending the evaporation will be independent of the amount of evaporated liquid because the molar entropies of vapour and liquid will remain constant. Therefore, the derivative $\partial S/\partial v$ will be equal to the ratio of the finite changes:

$$\frac{\partial S}{\partial v}=\frac{\Delta S_{\text{evap}}}{\Delta v_{\text{evap}}}=\frac{\underline{S}_{\text{vap}}-\underline{S}_{\text{liq}}}{\underline{v}_{\text{vap}}-\underline{v}_{\text{liq}}} \tag{4.63}$$

where the symbols $\underline{S}$ and $\underline{v}$ represent, as before, the molar values of the corresponding quantities. Calculating ΔS_{evap} by the second law (3.48) and rearranging, we obtain:

$$\Delta H_{\text{evap}}=T_{\text{evap}}\,(\underline{v}_{\text{vap}}-\underline{v}_{\text{liq}})\left(\frac{\partial p}{\partial T}\right)_{v} \tag{4.64}$$

In this equation $\partial p/\partial T$ expresses the dependence of the saturated vapour pressure on temperature. Since p_{sat} is independent of the volume, we may drop the subscript v signifying the constancy of the volume and write the usual derivative:

$$\Delta H_{\text{evap}}=T_{\text{evap}}\,(\underline{v}_{\text{vap}}-\underline{v}_{\text{liq}})\,\frac{dp}{dT} \tag{4.65}$$

This is the famous Clausius-Clapeyron equation as applied to the transition liquid $\rightleftarrows$ vapour. It was first derived in 1834 by Clapeyron and proved to be the first physico-chemical application of what we now call the second law of thermodynamics. In practically the same form, Eq. (4.65) can be applied to any other phase transition*. This problem will be examined in more detail in Chapter 5 (Sec. 5.1) where the Clausius-Clapeyron equation will be derived but in a somewhat different way.

Thus, each of the functions listed at the beginning of this section has two natural variables of which it will be characteristic. Recalling the conclusions (contained in Table 4.1), it should be noted now that any one of these functions can be used for the formulation of criteria of spontaneity and equilibrium for systems capable of existing with the variables natural for that function being kept constant. For functions having the dimensions of energy (U, H, F, G) tye criterion of spontaneity, as we already know, is their decreash; and the criterion of equilibrium is at a minimum. For the entrope which may also be regarded as a characteristic function of the variables U and v (or H and p) the corresponding criteria will be an increase in S and its maximum value.

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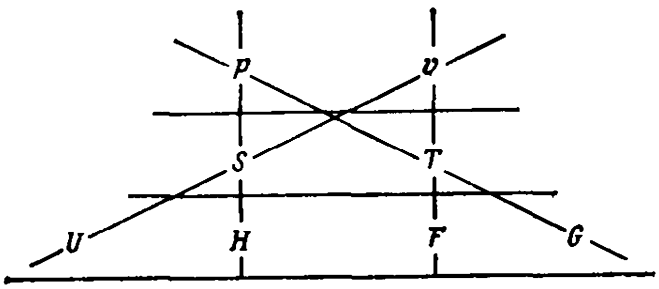
* Phase transitions of the first kind (first-order transitions) are meant here.

In concluding this section*, we shall give a figure which will help the reader to remember the natural variables of this or that function. *The required combination of symbols is found by cutting the figure with straight lines:*



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[*] In studying open multicomponent systems (see Chapter 1, Sec. 1.2) use is also made of the thermodynamic potential J defined by

$$J \doteq U - TS - \sum_{i=1}^{k} \mu_i n_i$$

where μ_i is the chemical potential of component i; k is the number of components; n_i is the number of moles. The potential J is a characteristic function of the temperature, volume and chemical potentials.

Chapter 5

Gibbs Free Energy and Equilibria in Physico-Chemical Systems

5.1. First-Order Phase Transitions

As has already been said (see Chapter 1), in physical chemistry use is often made of the term "phase" in different senses. In this section, which is devoted to the simplest phase equilibria, the term "phase" is defined as *those parts of a system which have thermodynamic properties, either identical or continuously varying from point to point, and which are separated from the rest of the system by boundary surfaces.*

For example, in dealing with the coexistence of liquid and vapour the entire liquid, i.e., its main bulk at the bottom of the vessel, and also the drops that may appear on the walls and lid of the vessel, is regarded as a single liquid phase. The vapour is the second phase. A liquid solution or a mixture of gases is a single phase. A mixture of crystals of two substances involves two phases. If two substances crystallize together, forming a solid solution, there is also formed a single phase.

If a system contains only one phase, it is often called *homogeneous*; if there are two or more phases, one speaks of a *heterogeneous* system.

The term "component" is also often used. At this point* we shall limit ourselves to defining a component as a substance (or substances) that makes up a system. In this section, we shall deal with one-component systems, i.e., systems consisting of a single substance, say, of water only or of carbon only. Every substance may be in three states of aggregation: the solid, liquid, or vaporous (gaseous) state. In a certain set of conditions, i.e., temperature and pressure, a substance can exist in two or three states of aggregation simultaneously, each of the states forming a separate phase. Here, as has already been mentioned, we are speaking of the equilibrium between phases in one-component systems, i.e., equilibria of the following types:

$$\begin{aligned} \text{liquid} &\rightleftharpoons \text{vapour} \\ \text{solid} &\rightleftharpoons \text{vapour} \\ \text{solid} &\rightleftharpoons \text{liquid} \end{aligned}$$

and some others.

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* A more extended definition of the term *component* is given in Chapter 8 concerned with the Gibbs phase rule.

A study of equilibria is carried out with the aid of the Gibbs free energy G which is known to be a characteristic function of temperature and pressure. Its exact differential for a system comprised of one individual substance is expressed as follows:

$$dG = -S\,dT + v\,dp \tag{5.1}$$

In what follows it is useful to apply this relation to one mole of substance, using the symbols $\underline{G}$, $\underline{S}$, and $\underline{v}$ for the molar values of the extensive properties. Then, on the basis of Eq. (5.1) and Sec. 4.2 we can write the derivatives:

$$\left(\frac{d\underline{G}}{dp}\right)_T = \underline{v} \tag{5.2}$$

and

$$\left(\frac{\partial \underline{G}}{\partial T}\right)_p = -\underline{S} \tag{5.3}$$

Relation (5.2) shows that the molar volume of a substance, $\underline{v}$, is a measure of the dependence of the Gibbs free energy on pressure at constant temperature. Since the volume is an essentially positive quantity, the derivative (5.2) is always larger than zero, i.e., the Gibbs free energy of the substance invariably increases with increasing pressure.

If we take, for example, one mole of hydrogen under standard conditions (1 atm, 298.15 K), the derivative (5.2) will assume the form

$$\left(\frac{\partial \underline{G}}{\partial p}\right)_T = \underline{v} = 24.453 \text{ litre/mole} = 24.453 \text{ litre}\cdot\text{atm/atm}\cdot\text{mole} \tag{5.4}$$

If we now convert litre·atmosphere to calories by multiplying by 24.2, we obtain, for one mole of hydrogen, a measure of increase of its molar Gibbs free energy per 1 atm: $(\partial \underline{G}/\partial p)_T = 591.8$ cal/mole × × atm. From Eq. (5.4) it follows that the Gibbs free energy of a substance depends on the pressure the more strongly, the larger the volume it occupies.

The derivative (5.3), on the other hand, shows a decrease in the molar Gibbs free energy with an increase in temperature; the entropy is a quantity which is always positive, and therefore the derivative (5.3) is always negative. If we refer again to one mole of hydrogen in standard conditions, the measure of the variation of its Gibbs free energy under these conditions will be the standard entropy:

$$\left(\frac{\partial \underline{G}}{\partial T}\right)_p = -\underline{S}^\circ_{298} = -31.208 \text{ cal/deg}\cdot\text{mole}$$

The molar Gibbs free energies play an important role in the study of equilibria under the conditions of constant temperature and pressure. And this is in spite of our failure to determine the absolute values of G as well as the absolute values of other properties having the dimensions of energy, i.e., U, H, and F.

Let us now consider in more detail the equilibrium between a liquid and its vapour. Suppose again we have a cylinder with a piston (Fig. 5.1) immersed in a thermostat. There is some liquid at the bottom of the cylinder and a vapour above it, which is in equilibrium with the liquid. The saturated vapour pressure is balanced by an external pressure created by loading the piston. The entire system is thus maintained at constant pressure and temperature. To the equilibrium in such a system, as known from Sec. 4.1, there corresponds a minimum of the Gibbs free energy or

$$dG_{T,p} = 0 \qquad (5.5)$$

which means that the Gibbs free energy of an equilibrium system remains unchanged upon transformation of an infinitesimal amount of vapour into liquid or of liquid into vapour.

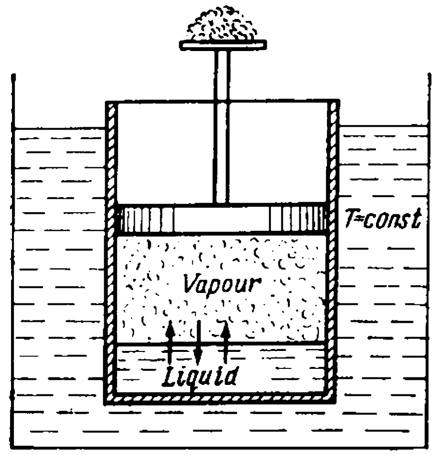

Fig. 5.1. The liquid-vapour equilibrium.

However, as experiment shows, the properties of liquid and vapour do not depend on their relative amounts, which are in equilibrium, and therefore the condition (5.5) can be replaced by the equality of the finite difference to zero:

$$\Delta G_{T,p} = 0$$

If we introduce the molar or specific Gibbs free energies of liquid and vapour, the condition (5.5) may be written in the form $\underline{G}_{\text{vap}} - \underline{G}_{\text{liq}} = 0$ or

$$\underline{G}_{\text{vap}} = \underline{G}_{\text{liq}} \qquad (5.6)$$

Hence, under equilibrium conditions the molar Gibbs free energies of liquid and vapour are equal and the equilibrium change from liquid to vapour or vice versa in any amount, which can be attained by the slow (infinitely slow) displacement of the piston, will not cause a change in the Gibbs free energy of the system until there is liquid and vapour.*

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* A phase transition of the type liquid $\rightleftharpoons$ vapour should be looked upon as an indifferent equilibrium with an extremely planar (horizontal) minimum. In mechanics, it is approximately equivalent to a sphere resting on a horizontal plane.

What happens when an attempt is made to displace the equilibrium by increasing the pressure. Suppose that we have succeeded in increasing the pressure in the system by an amount dp, i.e., up to $p_{sat} + dp$, by reducing the volume rapidly. In this case, according to Eq. (5.2) the molar Gibbs free energies of liquid and vapour undergo change:

$$\left(\frac{\partial \underline{G}_{liq}}{\partial p}\right)_T = \underline{v}_{liq} \quad \text{and} \quad \left(\frac{\partial \underline{G}_{vap}}{\partial p}\right)_T = \underline{v}_{vap} \tag{5.7}$$

But, generally speaking, except for the critical point, the molar (or specific) volume of the vapour is larger than the molar volume of the liquid, i.e., $\underline{v}_{vap} > \underline{v}_{liq}$, and, hence, the molar Gibbs free energies of the vapour and liquid change differently—they both increase but $\underline{G}_{vap}$ increases to a greater extent. As a result, there appears the inequality

$$\underline{G}'_{vap} > \underline{G}'_{liq} \tag{5.8}$$

which corresponds to the non-equilibrium state of the system in question. What will happen then? A part of vapour will undergo condensation, the pressure will decrease to p_{sat}, and the Gibbs free energies will become equal again, as in Eq. (5.6).

If the temperature of the system liquid $\rightleftharpoons$ vapour is raised by dT, then, according to Eq. (5.3), the Gibbs free energies of vapour and liquid will diminish, but since the entropy of vapour is greater than that of liquid, for this new non-equilibrium state we can write the inequality

$$\underline{G}''_{liq} > \underline{G}''_{vap} \tag{5.9}$$

When the equilibrium is restored, part of the liquid will evaporate, as a result of which the saturated vapour pressure will increase but the Gibbs energy of the vapour will increase to a greater extent than that of the liquid. As a result, to the new state of equilibrium at a higher temperature and pressure there will correspond the equality

$$\underline{G}'''_{liq} = \underline{G}'''_{vap}$$

in which the molar Gibbs free energies differ from the previous values.

What has been said above may serve as an illustration of the well-known Le Châtelier-Braun principle which states that *whenever stress is placed on any system in a state of equilibrium, the system will always react in a direction which will tend to counteract the applied stress.*

Let us now derive the Clausius-Clapeyron equation on the basis of the equilibrium condition (5.6). Suppose that the temperature and pressure in the system are changed by dT and dp, respectively.

For a new state of equilibrium in the system liquid $\rightleftharpoons$ vapour we can write the equality of the altered Gibbs free energies:

$$\underline{G}_{\text{vap}} + d\underline{G}_{\text{vap}} = \underline{G}_{\text{liq}} + d\underline{G}_{\text{liq}} \tag{5.10}$$

or, taking cognizance of Eq. (5.6),

$$d\underline{G}_{\text{vap}} = d\underline{G}_{\text{liq}} \tag{5.11}$$

Replacing the differentials of G with the aid of relation (5.1), we obtain

$$-\underline{S}_{\text{vap}}\, dT + \underline{v}_{\text{vap}}\, dp = -\underline{S}_{\text{liq}}\, dT + \underline{v}_{\text{liq}}\, dp \tag{5.12}$$

where $\underline{S}_{\text{vap}}$, $\underline{S}_{\text{liq}}$ and $\underline{v}_{\text{vap}}$, $\underline{v}_{\text{liq}}$ express, respectively, the molar entropies and volumes of the vapour and liquid. Rearranging expression (5.12), we obtain

$$\underline{S}_{\text{vap}} - \underline{S}_{\text{liq}} = \Delta S_{\text{vapn}} = (\underline{v}_{\text{vap}} - \underline{v}_{\text{liq}}) \frac{dp_{\text{sat}}}{dT} \tag{5.13}$$

But the change in entropy upon vaporization of one mole of liquid is equal, according to Eq. (3.48), to $\Delta H_{\text{vapn}}/T_{\text{vapn}}$. Therefore, we finally obtain the Clausius-Clapeyron equation:

$$\Delta H_{\text{vapn}} = T_{\text{vapn}} (\underline{v}_{\text{vap}} - \underline{v}_{\text{liq}}) \frac{dp_{\text{sat}}}{dT} \tag{5.14}$$

which exactly coincides with Eq. (4.65) derived earlier with the aid of the Maxwell relation.

The Clausius-Clapeyron equation is a very useful tool in the hands of an experienced physical chemist, enabling him to perform various kinds of calculations. Perhaps, the most surprising is the possibility of calculating a calorimetric quantity—the heat of vaporization—from the vapour pressure, i.e., data which are, in essence, mechanical.

Consider the following example of the approximate utilization of Eq. (5.14). The water vapour pressure at temperatures 99.5 and 100.5°C is equal, respectively, to 746.52 and 773.69 mm Hg. We use these data for calculating the derivative:

$$\frac{dp}{dT} \approx \frac{\Delta p}{\Delta T} = \frac{773.69 - 746.52}{100.5 - 99.5} = 27.17 \text{ mm Hg/deg} = 0.03575 \text{ atm/deg}$$

The molar volumes are taken at the average temperature, i.e., 100°C, $\underline{v}_{\text{vap}} = 30.109$ litres/mole and $\underline{v}_{\text{liq}} = 0.018$ litre/mole. Substituting these data into Eq. (5.14), we obtain:

$$\Delta H_{\text{vapn}} = 373.15.(30.109 - 0.018) \times 0.03575 = 401.47 \text{ litres·atm/mole}$$

In order to convert the heats of vaporization to more ordinary units, calories, we multiply by 24.2 and obtain $\Delta H_{\text{vapn}} = 9715.5$ cal/mole as the heat of vaporization of water at 100°C. In special tables one can find a more accurate value, 9710 cal/mole. It shows that an approximate calculation based only on two vapour pressure values and, basically, a single volume (the volume of liquid water is vanishingly small) nevertheless gave a value for the heat of vaporization very close to the correct value.

Evidently, in the resulting equation (5.14) there will be no change if we repeat the conclusion for any other phase equilibrium, say

$$\text{solid} \rightleftharpoons \text{vapour}$$

Naturally, here we are dealing with the heat of sublimation ΔH_{sub} and with the molar volume of a substance in the solid state, $\underline{v}_{\text{sld}}$. In both cases, the volume of the vapour is, as a rule, much greater than volume of the condensed phase, which may often be neglected; we may thus write approximately:

$$\Delta H_{\text{vapn}} = T\underline{v}_{\text{vap}} \frac{dp_{\text{sat}}}{dT} \quad (5.15)$$

or

$$\frac{dp_{\text{sat}}}{dT} = \frac{\Delta H_{\text{vapn}}}{T\underline{v}_{\text{vap}}} \quad (5.16)$$

As can easily be understood, the derivative dp_{sat}/dT is always greater than zero, since there are only positive quantities on the right-hand side of Eq. (5.16). Hence, the saturated vapour pressure, i.e., the pressure of the vapour in equilibrium with a liquid or a solid, increases with increasing temperature. Some relevant data are presented in Table 5.1 and in Fig. 5.2. If the vapour pressure is not too great, it is probably expedient to make use of the expression for the volume of the vapour with the aid of the ideal-gas equation*, i.e.,

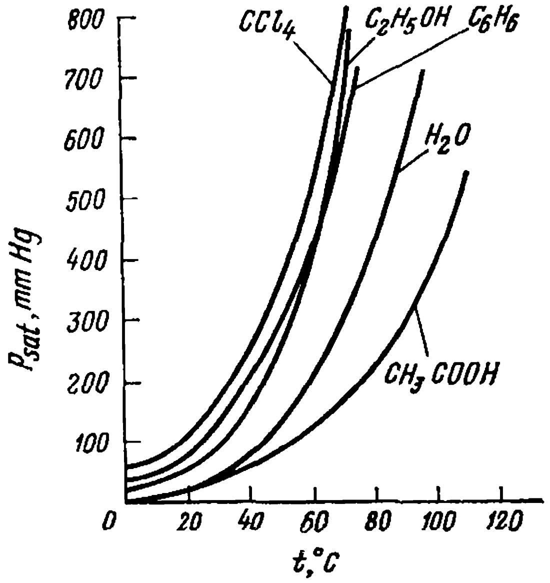

Fig. 5.2. Temperature dependence of the saturated vapour pressure of some liquids.

$$\underline{v}_{\text{vap}} = \frac{RT}{p_{\text{sat}}} \quad (5.17)$$

Substituting Eq. (5.17) into Eq. (5.16), we obtain the Clausius-Clapeyron equation in the following approximate form:

$$\frac{d \ln p_{\text{sat}}}{dT} = \frac{\Delta H_{\text{vapn}}}{RT^2} \quad (5.18)$$

---

* This does not in the least mean that the saturated vapour obeys completely the ideal-gas laws. To a given temperature there correspond quite definite values of the saturated vapour pressure and the vapour volume. But, first, using ideal-gas equations, we can determine approximately the vapour volume at a specified temperature and the corresponding pressure. Second, if we consider, at a single temperature, a number of substances with different vapour pressures, then we may speak, in an approximate way, of the indirectly proportional dependence of molar vapour volumes on pressure.

Relationships of this kind are widely used in thermodynamics and generally in physical chemistry. As will be seen at a later time (Sec. 5.10), the chemical equilibrium constant depends on temperature in a similar way.*

TABLE 5.1. **The Vapour Pressure of Selected Liquids at Various Temperatures, mm Hg**

Temperature, °C	CCl_4	C_2H_5OH	CH_3COOH	C_6H_6	H_2O
0	32.9	12.7	3.5	25.3	4.6
10	56.0	24.2	6.4	45.2	9.2
20	91.0	44.5	11.8	75.6	17.5
30	142.3	78.5	20.1	120.2	31.8
40	214.8	133.7	34.2	183.6	55.3
50	314.4	219.9	56.3	271.4	92.5
60	447.4	350.2	88.3	390.1	149.4
70	621.1	541.1	137.9	547.4	233.7
80	843.3	812.9	202.3	753.6	355.1
90	1122.0	1187.0	292.7	1016.1	525.8
100	1463.0	1693.0	417.0	1344.3	760.0

The well-known Arrhenius equation leads to the same form of the dependence in chemical kinetics. Of course, these coincidences are not accidental and serve as an indication of the general interrelationship of the phenomena.

Multiplying Eq. (5.18) by dT and integrating, we have:

$$\ln p_{\mathrm{sat}} = \frac{1}{R} \int \frac{\Delta H_{\mathrm{vapn}}}{T^2} dT + i \tag{5.19}$$

The integration constant i (or a quantity similar to it) was formerly known as the *chemical constant* (W. Nernst) and played an important role in calculations of the chemical equilibrium. At present it should be regarded only as a constant in the equation expressing the dependence of the vapour pressure on temperature. In order to integrate Eq. (5.19) one should know the dependence of the enthalpy of vaporization on temperature. The more general formulas derived by using this dependence will be written at a later time; at this point we put, at a first approximation, ΔH_{vapn} = const, which, as known from Kirchhoff's equation (2.120) or (2.121), corresponds to the assumption that the heat capacities of vapour and liquid are equal. Passing to the decimal logarithm, we obtain:

$$\log p_{\mathrm{sat}} = -\frac{\Delta H_{\mathrm{vapn}}}{4.576\, T} + \frac{i}{2.303} \tag{5.20}$$

---

* With the only difference, however, that the ΔH of reaction may have either of the signs, whereas here we have only the plus sign.

This formula is conveniently written in the form

$$\log p_{\text{sat}} = -\frac{A}{T} + B \tag{5.21}$$

where A and B are constant quantities for a given substance within the assumptions adopted.

Formula (5.21) points to the linear dependence of $\log p_{\text{sat}}$ on the inverse temperature; despite all the approximations, this dependence is justified over rather wide temperature and pressure ranges. Figure 5.3 shows several straight-line graphs for a number of liquids.

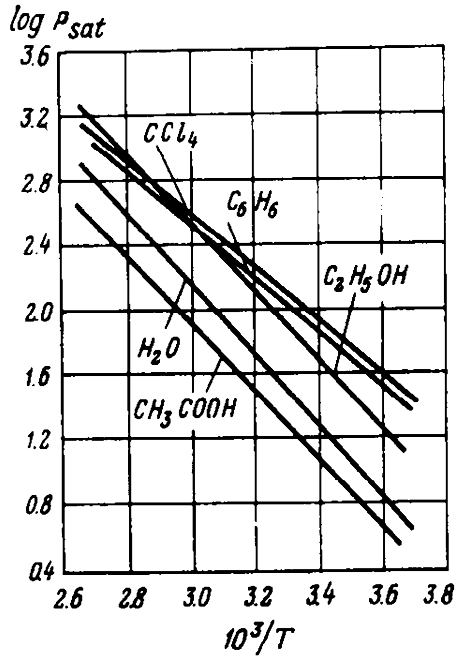

Fig. 5.3. Linear dependence of $\log p_{\text{sat}}$ on the inverse temperature for some liquids.

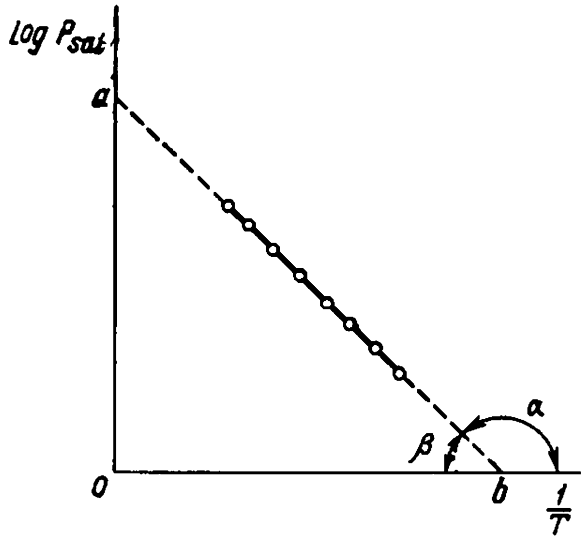

Fig. 5.4. Graphical determination of the heat of vaporization ΔH_{vapn} from the dependence of the vapour pressure on temperature.

Graphs of this type can be conveniently used for interpolation and extrapolation calculations and also for approximate calculations of the heat of vaporization. Figure 5.4 shows how this is done. A straight line plotted from experimental data is continued until it intersects the coordinate axes. According to Eq. (5.21), the intercept $\overline{oa}$ on the ordinate is equal to the constant B, and the slope of the straight line $\tan\alpha = -\tan\beta = -A$. Thus,

$$\tan\beta = \frac{\overline{oa}}{\overline{ob}} = A = \frac{\Delta H_{\text{vapn}}}{4.576} \tag{5.22}$$

Equation (5.18) is sometimes integrated at a first approximation from T_1 to T_2 and from p_1 to p_2 and the following formula is obtained:

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vapn}}}{4.576} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{5.23}$$

which is suitable for the calculation of one of the five quantities if the other four are known. For instance, if we know the heat of vaporization and the vapour pressure at a single temperature, we can calculate the vapour pressure at another, specified temperature.

For more accurate calculations one should have integrated Eq. (5.19), taking into account the dependence of the heat of vaporization on temperature. This dependence is described by Kirchhoff's equation, which is known to express the dependence of the heat of reaction on temperature:

$$\Delta H_T = \Delta H_J + \int (C_{\text{vap}} - C_{\text{liq}})\, dT \tag{5.24}$$

The use of Kirchhoff's equation in a precise form is complicated by the fact that in the liquid-vapour system at equilibrium the pressure is inevitably changed with temperature.

Therefore, C_{vap} and C_{liq} are not heat capacities at constant pressure. This refers particularly to the vapour. If we put approximately $C_{\text{vap}} - C_{\text{liq}} = C_{p\,(\text{vap})} - C_{p\,(\text{liq})} = \Delta C_p$, then Eq. (5.20) will assume the form:

$$\log p_{\text{sat}} = -\frac{\Delta H_J}{4.576\, T} + \frac{1}{4.576} \int \frac{\int \Delta C_p\, dT}{T^2}\, dT + \frac{i''}{2.303} \tag{5.25}$$

We shall call this relation the third-approximation formula; in this formula ΔH_J is a constant which must be calculated separately, for example, from a single value of the heat of vaporization, or graphically, and i'' is, as before, the integration constant.

If we set $\Delta C_p = \text{const}$ in Eq. (5.25), i.e., if we assume that the heat capacities of vapour and liquid are independent of temperature, we shall obtain a relation which may be called the second-approximation formula:

$$\log p_{\text{sat}} = -\frac{\Delta H_J}{4.576\, T} + \frac{\Delta C_p}{1.987} \log T + \frac{i'''}{2.303} \tag{5.26}$$

This formula is less accurate than Eq. (5.25) but more accurate than Eq. (5.20).

Sometimes, instead of the formulas given here, (5.25) and (5.26), which are eventually semi-empirical in character, the temperature dependence of the vapour pressure is often described by purely empirical relationships in the form of temperature power series.

For example, for diethyl ether at temperature below 273°K Taylor and Smite established the following formula (the pressure is expressed in mm Hg):

$$\log p = -\frac{2168.599}{T} + 13.882702 - 1.814165 \times 10^{-2} T + 1.718195 \times 10^{-5} T^2 \tag{5.27}$$

Using this relation and also the specific volumes of the gaseous and liquid ether at $-30°C$, namely, $v_{vap} = 5515.5$ and $v_{liq} = 1.3004$ ml/g, let us find the heat of vaporization of the ether at the temperature indicated, 243.15°K. To this end, one should first find the value of the derivative

$$\frac{dp}{dT}=p\frac{d\ln p}{dT} \tag{5.28}$$

Substituting first the specified temperature, $T = 243.15°K$, into Eq. (5.27), we find $\log p = 1.56458$ or $p = 36.6935$ mm Hg. Differentiating then Eq. (5.27) with respect to temperature, we obtain:

$$\frac{d\log p}{dT}=\frac{2168.599}{T^2}-1.814165\times 10^{-2}+3.43639\times 10^{-5}T$$

which gives $d\log p/dT = 0.0269341$ for $T = 243.15°K$. Then, from Eq. (5.28) we can find the sought-for derivative:

$$\frac{dp}{dT}=36.6935\times 2.303\times 0.0269341=2.275614 \text{ mm/deg}=0.002994 \text{ atm/deg}$$

We shall now use the Clausius-Clapeyron equation in the exact differential form (5.14):

$$\Delta H_{vapn}=T\,(v_{vap}-v_{liq})\frac{dp}{dT}=$$

$$=243.15\times 5.5142\times 0.002994=4.0118 \text{ litre·atm/g}=97.08 \text{ cal/g} \tag{5.29}$$

What has just been said about the equilibrium between liquid and vapour is also valid for sublimation.

The Clausius-Clapeyron equation is applicable to any phase transition of the first kind. Besides the equilibria mentioned above, i.e., the equilibria liquid $\rightleftharpoons$ vapour or solid $\rightleftharpoons$ vapour, we may also consider the equilibrium between a solid and a liquid, i.e.,

$$\text{solid} \rightleftharpoons \text{liquid} \tag{5.30}$$

which occurs at the melting and freezing point, and also the equilibrium between various crystal modifications of a solid:

$$\text{solid (I)} \rightleftharpoons \text{solid (II)} \tag{5.31}$$

Examples are the equilibria between rhombic and monoclinic sulphur and between graphite and diamond. For the equilibrium (5.30) the Clausius-Clapeyron equation assumes the form

$$\Delta H_{melt}=T_{melt}\,(\underline{v}_{liq}-\underline{v}_{sld})\frac{dp}{dT} \tag{5.32}$$

The derivative on the right-hand side of the equation expresses the dependence of the equilibrium pressure on temperature, which, as has already been said, is the melting point. It would be more spectacular to invert the derivative and to consider the dependence of the melting point on pressure. Solving Eq. (5.32) for dT/dp, we obtain:

$$\frac{dT_{melt}}{dp}=\frac{T_{melt}\,(\underline{v}_{liq}-\underline{v}_{sld})}{\Delta H_{melt}} \tag{5.33}$$

This expression differs essentially from Eq. (5.14) in that the molar volumes are comparable here and, generally speaking, two cases can be distinguished. For most substances $\underline{v}_{\text{liq}} > \underline{v}_{\text{sld}}$ and therefore the derivative in Eq. (5.33) is greater than zero and the melting temperature increases with increasing pressure. However, for some substances, of which water is the most widely used, $\underline{v}_{\text{liq}} < \underline{v}_{\text{sld}}$, and the melting temperature decreases with increasing pressure.

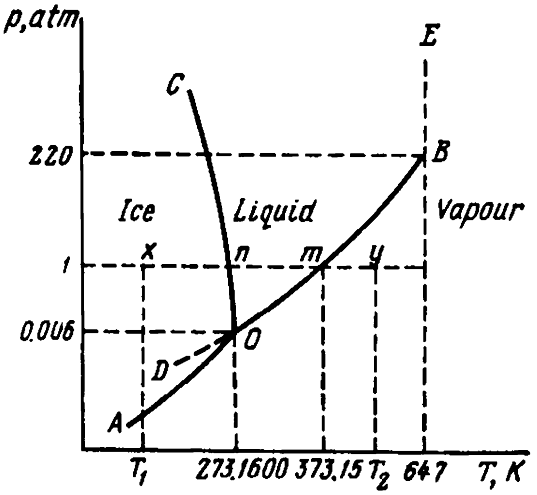

Fig. 5.5. Phase diagram for water at moderate pressures.

Let us calculate dT_{melt}/dp for ice. The specific volumes of liquid water and ice are, respectively, equal to 1.0001 and 1.0908 cm³/g, the specific heat of melting (fusion) being equal to $\Delta H_{\text{melt}} = 79.7$ cal/g. Hence, from Eq. (5.33), we have:

$$\frac{dT_{\text{melt}}}{dp} = -\frac{273.15 \times 0.0907}{79.7 \times 41.3} = $$

$$= -0.00753 \text{ deg/atm}$$

that is, as the pressure is raised by 1 atm the melting point of ice decreases by about 0.0075°, a seemingly insignificant amount; however, at high pressures the decrease of T_{melt} becomes rather appreciable and at 2100 atm the melting temperature falls to about —20°C. Figure 5.5 shows the phase diagram of water for the region of moderate pressures. It should perhaps be considered by starting from the curve *OC* which represents the dependence of the melting point of ice (ordinary ice) on pressure. The slope of the curve *OC* to the left is evidence of the negative value of the derivative dT_{melt}/dp. The point *O* is called the triple point; its coordinates 273.16°K and 0.006 atm (4.58 mm Hg) correspond to the only conditions of coexistence of water in all the three states of aggregation of water—liquid, solid and vapour. The temperature 273.16°K is the melting point of ice at the saturated water vapour pressure. This point is above 0°C. The zero temperature on the Celcius scale is known to be the melting point at 1 atm pressure. The line in question is terminated at a pressure of about 2100 atm and a temperature of about —20°C, which is the lowest melting point of ordinary ice. At pressures above 2100 atm the hexagonal structure of ordinary ice (ice I) rearranges, that is, undergoes a phase transition, to another crystalline modification known as ice III. This will be considered in more detail later (see Fig. 5.7). The line *OB* expresses the dependence of the saturated vapour pressure of liquid water on temperature. It originates at the triple point and terminates at the critical point (374°C and 220 atm). On careful cooling of pure water, however, a supercooled state results. The broken line *OD* corresponds to the vapour pressure above such supercooled metastable water, i.e., water which is in an unstable state. This curve is located above the line *AO*, which expresses the dependence of the vapour pressure above ice. In this region (i.e., to the left of the point *O*) liquid water must transform spontaneously to the solid state and this transition will be accompanied by a loss in the Gibbs free energy.* The line *AO* cannot be extended into the unstable region to the right of the point *O*, i.e., the solid cannot be overheated above the melting point. Thus, the line *AO* ends at the triple point. It may be assumed to originate at absolute zero.

The lines *AO*, *OB*, and *OC* divide the area of the diagram into 3 regions of existence of water in various states of aggregation. The region situated below the lines *AOB* is the region of existence of vapour; that above the lines *COB* is the liquid region, and that above and to the left of the lines *AOC* is the region of ordinary ice. Thus, moving along the horizontal broken line from point x to point y will involve further conversions. At point x at 1 atm pressure and temperature T_1 ice is stable. The movement along the horizontal line to the right will mean its heating, which extends to point n. Here the increase of temperature is stopped: as the heat supply is continued the isothermal phase transition ice $\rightleftarrows$ water occurs. When ice melts completely, the representative point keeps moving to the right, which means that liquid water is being heated. At point m water boils at 100°C and this temperature will remain constant until the entire amount of water is vaporized. Further, from points m to point y it is the vapour that will be heated to T_2. In the diagram of Fig. 5.5 one more region can be singled out—it is the region of the gas, which is located to the right of the vertical line *BE*, i.e., at temperatures above the critical temperature. As known, a substance in this state cannot be converted to the liquid state by compression and therefore it should be called a gas, differentiating it from a vapour, at least an unsaturated vapour.

From what has been said above it follows that water belongs to the category of a few substances** whose volume in the solid state is greater than in the liquid state. In the case of water, this is associated with the loose hexagonal structure of crystals of ordinary ice. An approximate idea of such a structure can be furnished by means of a plane representation (Fig. 5.6). However, it shows the presence of large voids if the water molecules are regularly arranged in the hexagonal lattice. Upon melting the lattice is destroyed and a closer arrangement of the molecules becomes possible (Fig. 5.6*b*). Nevertheless, the units of the ordered hexagonal structure are still retained in the liquid state in the immediate vicinity of the melting point. This is evidently responsible for another, unique property of water—the decrease in volume upon heating from 0 to about 4°C.

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* Proceeding from the derivative $d\underline{G}/dp = \underline{v}$, we think that at low pressures $\underline{v} = RT/p$ and $d\underline{G} = RT\frac{dp}{p}$. At constant temperature $\Delta G = G_2 - G_1 = RT \ln \frac{p_2}{p_1}$. From this it follows that $\Delta G < 0$ at $p_2 < p_1$.

** For example, bismuth and gallium.

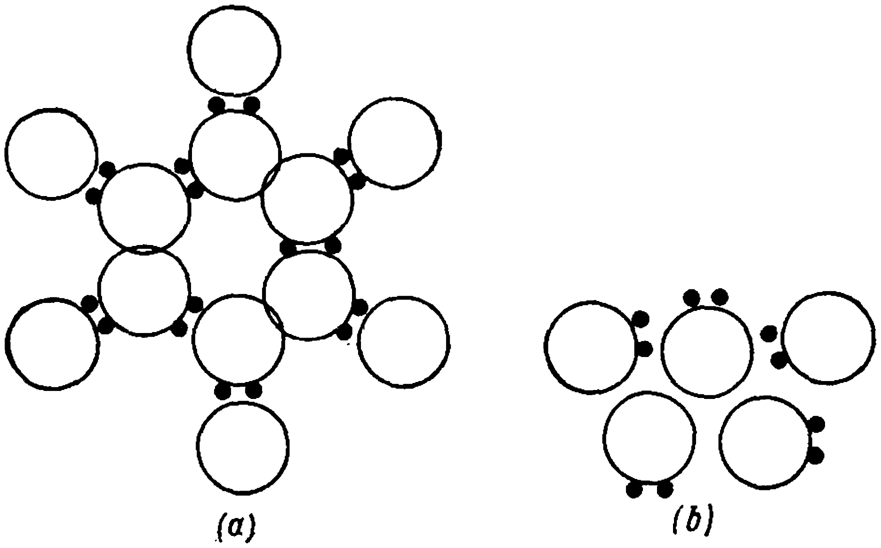

Fig. 5.6. Approximate plane representation of the molecular structure of water: *a*—"loose" hexagonal structure of ice I; *b*—liquid water; the unfilled circles represent oxygen atoms and the filled circles hydrogen atoms.

These specific features of water play an essential part in geological and biological processes. The expansion of water upon freezing in the fissures of rocks is one of the factors causing their breakdown. Having a lesser density, ice floats in water and thereby creates a heat-insulating sheath hindering the freezing of water basins down to the bottom. If ice had not possessed this property, biological and geological processes on the earth would have probably occurred in quite a different way.

At a pressure of above 2100 atm ordinary ice (ice I) is converted to other crystalline modifications of solid water. Figure 5.7 shows schematically the phase diagram of water at high pressures; it is an extension of the phase diagram in Fig. 5.5 to the region of high pressures; a common feature is that they both have the curve *OC*. The diagram in Fig. 5.7 is plotted on the basis of the works of Tamman and Bridgman. It shows that liquid water can also be found to be in equilibrium with ice of types III, V, VI and VII. The molar volumes of all these crystalline modifications are smaller than the molar volume of liquid water; therefore, their melting temperatures increase with increasing pressure. Especially interesting is ice VII, which is stable at a pressure of about 40,000 atm and a temperature of up to 190°C (there are no such data in Fig. 5.7). The region of ice II, as can be seen from the diagram, does not come into contact with the liquid water region—it can coexist only with the other solid modifications, I, III, and V. Ice IV is not shown in the diagram—it was observed but, as has been found, it is unstable under all the conditions studied.

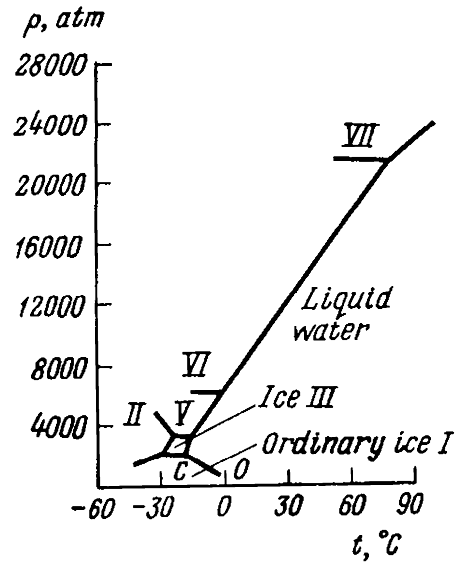

Fig. 5.7. Phase diagram for water at high pressures.

Let us now apply the general considerations concerning equilibrium which served as the basis for the derivation of the Clausius-Clapeyron equation to an equilibrium of the type (5.31)

$$\text{graphite} \rightleftharpoons \text{diamond} \quad (5.34)$$

The equilibrium between graphite and diamond sets in, just as in a general case, when the molar (gram-atom) Gibbs free energies are equal, $\underline{G}_{\text{graphite}} = \underline{G}_{\text{diamond}}$. Under ordinary conditions (1 atm, 298°K) they are not equal. Indeed, applying the expression $G = H - TS$ to the isothermal transition of the system from state I to state II, we can write the difference

$$\Delta G_T = \underline{G}_2 - \underline{G}_1 = \Delta H_T - T\Delta S_T \quad (5.35)$$

where ΔH_T is the heat of transition at constant pressure; ΔS_T is the corresponding entropy change. For the transition (5.34) it is known that $\Delta H^\circ_{298} = 453.2$ cal/mole. The entropies of graphite and diamond are also known: $S^\circ_{298} = 1.3609$ and $S^\circ_{298} = 0.5829$ eu (cal/deg·mole).

Thus, for the transformation of one gram-atom of graphite into diamond $\Delta S_T = -0.778$ cal/deg·mole. Hence, $\Delta G^\circ_{298} = \Delta H^\circ_{298} - 298.1 \times \Delta S^\circ_{298} = 453.2 + 298.15 \times 0.778 = 685$ cal/mole. In other words, under these conditions the conversion of graphite to diamond would have been associated with an increase in the Gibbs free energy. The reverse transformation must proceed spontaneously from a thermodynamic standpoint. This does not occur in practice because of the extremely low rate of the process, which can be speeded up by increasing the temperature.

We shall now calculate the pressure at which the Gibbs free energies of graphite and diamond are equal and, hence, these two modifications of carbon will be in equilibrium. We shall proceed from the derivative (5.2) which is written for both states:

$$\left(\frac{\partial \underline{G}_{\text{graphite}}}{\partial p}\right)_T = \underline{v}_{\text{graphite}}$$
$$\left(\frac{\partial \underline{G}_{\text{diamond}}}{\partial p}\right)_T = \underline{v}_{\text{diamond}} \qquad (5.36)$$

Subtracting the first relation from the second, we obtain

$$\left(\frac{\partial (\underline{G}_{\text{diamond}} - \underline{G}_{\text{graphite}})}{\partial p}\right)_T = \frac{\partial \Delta G}{\partial p} = \underline{v}_{\text{diamond}} - \underline{v}_{\text{graphite}} = \Delta v \qquad (5.37)$$

Taking cognizance of the constancy of temperature, we pass over to ordinary differentials:

$$d\Delta G = \Delta v dp \qquad (5.38)$$

Solving the problem involved, we integrate Eq. (5.38) between p_1 and p_2:

$$\Delta G_{p_2} - \Delta G_{p_1} = \int_{p_1}^{p_2} \Delta v \, dp \approx \Delta v (p_2 - p_1) \qquad (5.39)$$

assuming approximately that the difference of the molar volumes is independent of pressure. The pressure p_1 in Eq. (5.39) is equal to 1 atm; the corresponding ΔG has been found above (685 cal/mole); $\Delta v = \underline{v}_{\text{diamond}} - \underline{v}_{\text{graphite}} = -1.91$ cm^3/mole. What remains to do is to find the pressure p_2, for which $\Delta G_{p_2} = 0$:

$$p_2 - 1 = -\frac{\Delta G_{p_1}}{\Delta v} = -\frac{\Delta G^\circ_{298}}{\Delta v} = \frac{[685 \text{ cal/mole} \times 41.31] \text{ cm}^3\cdot\text{atm/mole}}{1.91 \text{ cm}^3\text{/mole}} =$$
$$= 14{,}815 \text{ atm} \quad \text{and} \quad p_2 = 14{,}816 \text{ atm}$$

Hence, at 25°C graphite is in equilibrium with diamond at a pressure of about 15,000 atm. At still higher pressures the transition graphite → diamond is accompanied by a loss of the Gibbs free energy, i.e., it becomes thermodynamically spontaneous. However, as experiment shows, at this temperature the thermodynamically possible recrystallization of graphite to diamond does not practically occur because of the extreme sluggishness of the process. To speed up the process it is necessary to raise the temperature, and this in turn leads to the necessity to increase the pressure even more. In practice, the recrystallization process is conducted in the presence of catalysts (Ni + Cr + . . .) at temperatures higher than 1500°C and at pressures of the order of 60,000 atm.*

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* In Chapter 8 we give a phase diagram for carbon (after Bundy).

5.2. Configurational Effects. Second-Order Phase Transitions. Ehrenfest's Equations

The equilibrium phase transitions considered above occur provided that the molar Gibbs free energies, or chemical potentials, of a substance in different phases are constant. At the same time, the entropy and the volume which are the first derivatives of the Gibbs free energy

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial p}\right)_T = v \tag{5.40}$$

undergo a discontinuous change. According to the terminology proposed by Ehrenfest (1933), it is because of this peculiarity that these transitions (or transformations) are called *transitions of the first kind* (*first-order transitions*). There exist, however, transformations in which the first derivatives of G do not change but the second derivatives change discontinuously; for example,

$$\begin{aligned} \frac{\partial^2 G}{\partial T^2} &= -\frac{\partial S}{\partial T} = -\frac{C_p}{T} \\ \frac{\partial^2 G}{\partial p\,\partial T} &= \frac{\partial v}{\partial T} = \alpha v \end{aligned} \tag{5.41}$$

where $\alpha = (1/v)(\partial v/\partial T)_p$ is the thermal expansion coefficient. The changes indicated are called, accordingly, *phase transitions of the second kind* (*second-order transitions*). In principle, it is also possible to define phase transitions of higher ranks in view of discontinuous changes in the third and higher derivatives.

Let us consider in more detail those transitions which are associated with the discontinuous changes of heat capacity and thermal expansivity and compressibility, i.e., the second derivatives.

Thus, for example, an equimolar alloy of copper and gold exhibits an anomalous behaviour near a certain temperature ($T \approx 710$°K). It is precisely at this point that the heat capacity of the alloy and the thermal expansion coefficient undergo a discontinuous change. The form of the curve for the heat capacity is shown in Fig. 5.8. The temperature at which this phenomenon is observed is called the *Curie point* by analogy with the temperature at which ferromagnetism disappears, a phenomenon studied by Pierre Curie. The peak shown in Fig. 5.8 resembles the Greek letter lambda, λ, and therefore the point corresponding to the peak on the temperature scale is called the *lambda point*. There is still another point, also known as the lambda point, which corresponds to the transition (liquid ^{4}HeI) $\rightleftharpoons$ (liquid ^{4}HeII) (see Chapter 8, Sec. 8.2).

In order to account for phenomena of this kind, we extend the concept of the heat capacity by introducing the concept of the configurational heat capacity. Just as in Chapter 2, we shall assume that the state of a system of fixed composition is determined by the variables T, p and ξ. Then the first law (2.73) will have the following form:

$$\delta Q = C_{p,\,\xi}\, dT + h_{T,\,\xi}\, dp + h_{T,\,p}\, d\xi \tag{5.42}$$

If the pressure alone is assumed to be constant, then, by dividing Eq. (5.42) by dT, we obtain the following definition of the heat capacity of a system of variable composition:

$$C_p \equiv \left(\frac{\delta Q}{\partial T}\right)_p = C_{p,\,\xi} + h_{T,\,p}\left(\frac{\partial \xi}{\partial T}\right)_p \tag{5.43}$$

where $C_{p,\,\xi}$ is the heat capacity of the system at constant pressure and composition, and the second term of the sum, which expresses the heat absorbed by the system as a result of the temperature dependence of its inner structure (configuration), is known as the *configurational heat capacity*:

$$C_p^{\text{conf}} = h_{T,\,p}\left(\frac{\partial \xi}{\partial T}\right)_p \tag{5.44}$$

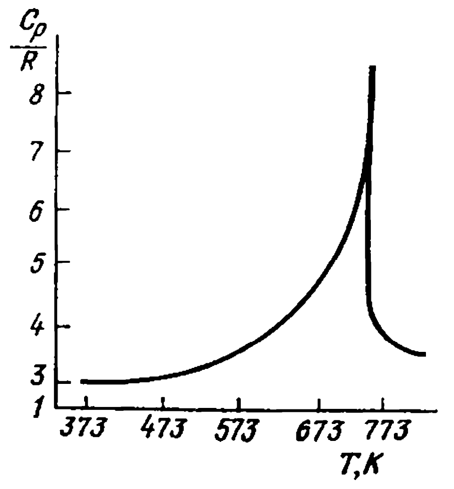

Fig. 5.8. The heat capacity of an equimolar alloy of copper and gold near the Curie point.

The nature of the variable ξ (which here we termed a chemical variable) may vary. In the case of an alloy of copper and gold it is associated with the disappearance of the so-called long-range order, in which case the atoms of copper and gold in the alloy lattice form, so to say, interpenetrating sublattices.

In connection with the problem under discussion, it should be noted that the heat capacity being measured may be dependent on the rate of the process. In a sufficiently slow process the change of ξ will follow the change in temperature and the transformation will occur under equilibrium conditions (the affinity* $A = 0$) and in Eq. (5.43) the heat capacity C_p will be equal to $C_{p,\,A=0}$. On the other hand, in a rapid process the variable ξ will not have time to follow the change in temperature and C_p will approach the lesser value of $C_{p,\,\xi}$.

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* The chemical affinity will be discussed in more detail in Sec. 5.3. By definition (5.75) the affinity $A = -(dG/d\xi)_{T,p} \approx -\Delta G_{T,p}$, i.e., expresses the differential dependence of the Gibbs free energy of the system on composition (i.e., the variable ξ). According to (4.21), $A = 0$ for an equilibrium transformation.

As has already been mentioned, at the lambda point not only the heat capacity but also the thermal expansion coefficient is discontinuous. Since this is also associated with configurational effects, these effects should be considered also from the standpoint of the thermal expansion coefficient α and the isothermal compressibility β.

Having chosen the variables T, p and ξ, we write the differential of the volume:

$$dv = \left(\frac{\partial v}{\partial T}\right)_{p,\,\xi} dT + \left(\frac{\partial v}{\partial p}\right)_{T,\,\xi} dp + \left(\frac{\partial v}{\partial \xi}\right)_{T,\,p} d\xi \tag{5.45}$$

Further, assuming the temperature to be constant ($dT = 0$), we assume that the change in volume also occurs with the chemical affinity being constant (A = const) and, dividing Eq. (5.45) by dp, we obtain the identity

$$\left(\frac{\partial v}{\partial p}\right)_{A,\,T} \equiv \left(\frac{\partial v}{\partial p}\right)_{T,\,\xi} + \left(\frac{\partial v}{\partial \xi}\right)_{T,\,p} \left(\frac{\partial \xi}{\partial p}\right)_{A,\,T} \tag{5.46}$$

On the other hand, according to the definition, the affinity $A = -(\partial G/\partial \xi)_{T,\,p}$ and $(\partial A/\partial p)_{T,\,\xi} = -\partial^2 G/\partial \xi \partial p = -(\partial v/\partial \xi)_{T,\,p}$; hence, relation (5.46) can be rewritten thus:

$$\left(\frac{\partial v}{\partial p}\right)_{A,\,T} = \left(\frac{\partial v}{\partial p}\right)_{T,\,\xi} - \left(\frac{\partial A}{\partial p}\right)_{T,\,\xi} \left(\frac{\partial \xi}{\partial p}\right)_{A,\,T} \tag{5.47}$$

On the basis of the general dependence of the affinity $A = A(T,\ p,\ \xi)$ we can write another identity, namely, if

$$dA = \left(\frac{\partial A}{\partial T}\right)_{p,\,\xi} dT + \left(\frac{\partial A}{\partial p}\right)_{T,\,\xi} dp + \left(\frac{\partial A}{\partial \xi}\right)_{T,\,p} d\xi \tag{5.48}$$

then, assuming again the affinity and temperature to be constant, we obtain the following relation by dividing by $d\xi$:

$$\left(\frac{\partial p}{\partial \xi}\right)_{A,\,T} = \left(\frac{\partial A}{\partial \xi}\right)_{T,\,p} \Big/ \left(\frac{\partial A}{\partial p}\right)_{T,\,\xi} \tag{5.49}$$

in which expression the derivative $(\partial A/\partial \xi)_{T,\,p} = (\partial^2 G/\partial \xi^2)_{T,\,p}$ expresses the dependence of the affinity on the chemical variable. We now substitute $(\partial A/\partial p)_{T,\,\xi}$ from Eq. (5.49) into Eq. (5.47):

$$\left(\frac{\partial v}{\partial p}\right)_{A,\,T} = \left(\frac{\partial v}{\partial p}\right)_{T,\,\xi} + \left(\frac{\partial A}{\partial \xi}\right)_{T,\,p} \left(\frac{\partial \xi}{\partial p}\right)^2_{A,\,T} \tag{5.50}$$

The last equation can be used, in particular, for a transition under equilibrium conditions when $A = 0$.

Next we determine the isothermal compressibility, first, for an equilibrium transition when with a change in pressure there occurs a process reflected in a change in ξ,

$$\beta_{A=0} = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_{A=0,\,T} \tag{5.51}$$

and, second, for the process of compression at constant ξ:

$$\beta_\xi = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,\,\xi} \tag{5.52}$$

Now, dividing Eq. (5.50) by the volume, we can write the following relation:

$$\beta_{A=0} = \beta_\xi + \frac{1}{v}\left(\frac{\partial A}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial p}\right)^2_{T,\,A=0} \tag{5.53}$$

which connects the two compressibilities. From Eq. (5.53) it is seen that since for the stable phase the derivative $(\partial A/\partial\xi)_{T,\,p}$ is always negative (this provides the return of the system to the initial state upon random displacement), the coefficient $\beta_{A=0}$ is always greater than β_ξ. In other words, for equal variations of the pressure under equilibrium conditions, when the transition reflected in a change in ξ immediately follows a change in the pressure, the volume decreases to a greater extent than in the case where the composition remains constant.

The two thermal expansion coefficients $\alpha_{A=0}$ and α_ξ can be determined in an analogous manner; the following relation may hold for them:

$$\alpha_{A=0} = \alpha_\xi + \frac{1}{v}\left(\frac{\partial A}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial p}\right)_{T,\,A=0}\left(\frac{\partial \xi}{\partial T}\right)_{p,\,A=0} \tag{5.54}$$

If we assume, as before, that the variable ξ reflects the change in the inner configuration of the system, as, for example, the disappearance of long-range order in the case of a copper-gold alloy, the second terms in Eqs. (5.53) and (5.54) will define, respectively, the *configurational compressibility* and the *configurational expansivity*:

$$\beta^{\text{conf}} = -\frac{1}{v}\left(\frac{\partial A}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial p}\right)^2_{T,\,A=0} = -\frac{1}{v}\left(\frac{\partial v}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial p}\right)_{T,\,A=0} \tag{5.55}$$

$$\alpha^{\text{conf}} = \frac{1}{v}\left(\frac{\partial A}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial p}\right)_{T,\,A=0}\left(\frac{\partial \xi}{\partial T}\right)_{p,\,A=0} = \frac{1}{v}\left(\frac{\partial v}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial T}\right)_{p,\,A=0} \tag{5.56}$$

We can now compare the various configurational effects on the basis of Eqs. (5.44), (5.55) and (5.56):

$$C_p^{\text{conf}}\beta^{\text{conf}} = vT\,(\alpha^{\text{conf}})^2 \tag{5.57}$$

In the last transformation we have made use of the relation

$$h_{T,\,p} = -T\left(\frac{\partial A}{\partial \xi}\right)_{T,\,p}\left(\frac{\partial \xi}{\partial T}\right)_{p,\,A=0}$$

which follows from the expression for the total differential of the affinity.

Let us now turn to the use of the configurational effects considered above for the derivation of Ehrenfest's equations which reflect the effect of pressure on the Curie point.

The well-known Clausius-Clapeyron equation for a phase transition of the first kind which was written earlier for a finite change ($\Delta\xi = 1$) in the ordinary form $\Delta H_{T,p} = T(v_2 - v_1)(dp/dT)$, can be put in differential form:

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,p} = h_{T,p} = T\left(\frac{\partial v}{\partial \xi}\right)_{T,p}\left(\frac{\partial p}{\partial T}\right)_{\xi} \tag{5.58}$$

or

$$\left(\frac{\partial p}{\partial T}\right)_{\xi} = \frac{h_{T,p}}{T\left(\frac{\partial v}{\partial \xi}\right)_{T,p}} \tag{5.59}$$

We multiply the numerator and denominator in Eq. (5.59) by the derivative $(\partial\xi/\partial T)_{p,A=0}$ and make use of Eqs. (5.44) and (5.56) to obtain the following relation:

$$\left(\frac{\partial p}{\partial T}\right)_{\xi} = \frac{h_{T,p}\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0}}{T\left(\frac{\partial v}{\partial \xi}\right)_{T,p}\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0}} = \frac{C_p^{\mathrm{conf}}}{T\times v\times\alpha^{\mathrm{conf}}} \tag{5.60}$$

Thus, the dependence $(dp/\partial T)_\xi$ is determined mainly by the configurational heat capacity and the configurational thermal expansion coefficient (configurational expansivity). We apply this dependence to the Curie point at which there is a point of discontinuity in the heat capacity (see Fig. 5.8) and in the thermal expansion coefficient. We assume that the discontinuity in these quantities is associated with a change of the internal configuration of the system at the Curie point. If the heat capacity and thermal expansion coefficient are denoted as C_p' and α' for one of the configurations and as C_p'' and α'' for the other, then the corresponding discontinuities (jumps) in the coefficients will be represented by the differences $C_p' - C_p''$ and $\alpha' - \alpha''$. Then, for the Curie point we can write $C_p^{\mathrm{conf}} = C_p' - C_p''$ and $\alpha^{\mathrm{conf}} = \alpha' - \alpha''$, and Eq. (5.60) now assumes the form of the *first Ehrenfest equation*:

$$\left(\frac{\partial p}{\partial T}\right)_{\xi=0} = \frac{C_p' - C_p''}{T_\lambda v_\lambda (\alpha' - \alpha'')} \tag{5.61}$$

The second Ehrenfest equation derives from the transformation of an identity which is valid for all equilibrium systems described by the variables T, p, ξ:

$$\left(\frac{\partial p}{\partial T}\right)_{\xi} = -\frac{\left(\frac{\partial \xi}{\partial T}\right)_p}{\left(\frac{\partial \xi}{\partial p}\right)_T} \tag{5.62}$$

Multiplying the numerator and denominator by $(\partial v/\partial \xi)_{T,\,p}$, we have:

$$\left(\frac{\partial p}{\partial T}\right)_{\xi} = -\frac{\left(\frac{\partial \xi}{\partial T}\right)_{p}\left(\frac{\partial v}{\partial \xi}\right)_{T,\,p}}{\left(\frac{\partial \xi}{\partial p}\right)_{T}\left(\frac{\partial v}{\partial \xi}\right)_{T,\,p}} = \frac{\alpha^{\text{conf}}}{\beta^{\text{conf}}} \tag{5.63}$$

Making use of Eq. (5.63) for the Curie point, we obtain the *second Ehrenfest equation*:

$$\left(\frac{\partial p}{\partial T}\right)_{\xi=0} = \frac{\alpha' - \alpha''}{\beta' - \beta''} \tag{5.64}$$

Apart from the changes in the properties during phase transitions of the second kind considered above, there is also observed a change in the electrical conductivity (the appearance of metallic superconduction at low temperatures), viscosity, optical properties, etc.

5.3. Thermodynamic Characteristics of a Chemical Reaction. Chemical Affinity

We write the equation of a general chemical reaction:

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightleftharpoons \nu_1' B_1' + \nu_2' B_2' + \ldots \tag{5.65}$$

where B_i represent the participants in the reaction; ν_i are the corresponding stoichiometric coefficients. Suppose that each of the reactants is placed in a separate vessel and is thus in a pure individual state under constant conditions, say, at constant p and T. Then, the reactants are mixed in some way in a vessel and are made to react; the products formed are separated and placed each in a separate vessel. We are not interested in how the entire procedure is carried out; our task is to compare the thermodynamic properties of the reactants and products. A comparison of the initial and final states is just the objective of chemical thermodynamics.

We assign the molar Gibbs free energy to each of the reactants, $\underline{G}_i$, and draw up the algebraic sum of the Gibbs energies corresponding to the conversion (5.65) of the reactants into the products:

$$\nu_1' \underline{G}_1' + \nu_2' \underline{G}_2' + \ldots - \nu_1 \underline{G}_1 - \nu_2 \underline{G}_2 - \ldots = G_{\text{II}} - G_{\text{I}} = \Delta G_T \tag{5.66}$$

where G_{II} and G_{I} are, respectively, the total Gibbs energies of the products and reactants; ΔG_T is the most important thermodynamic characteristic of the reaction. The quantity ΔG_T is called the Gibbs free energy change for the reaction or simply the Gibbs free energy of the reaction.* The subscript for ΔG_T implies that ΔG refers to any given constant temperature T. The importance of the quantity ΔG_T consists in that we can predict whether the reaction will occur spontaneously. The reaction can occur spontaneously at constant pressure* and temperature from a thermodynamic standpoint provided ΔG_T is less than zero.

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* By analogy with ΔH_T, which is called the reaction enthalpy.

Recall the physical significance of ΔG_T. According to Eq. (4.28), $-\Delta G$, i.e., the decrease in the Gibbs free energy, is equal to the maximum useful work, i.e., the work done by the system in an equilibrium process minus the work of expansion at constant pressure $p\,(v_2 - v_1)$. In a general form we can write for constant pressure and temperature:

$$W'_T \leqslant -\Delta G_T \tag{5.67}$$

that is, the useful work is equal to or less than the decrease in the Gibbs free energy in an equilibrium process. Most often the useful work is associated with the transfer of electrical charges, i.e., in short, this is electrical work. Its measurement forms the basis for one of the methods of direct determination of $(W')_{\max} = -\Delta G_T$.

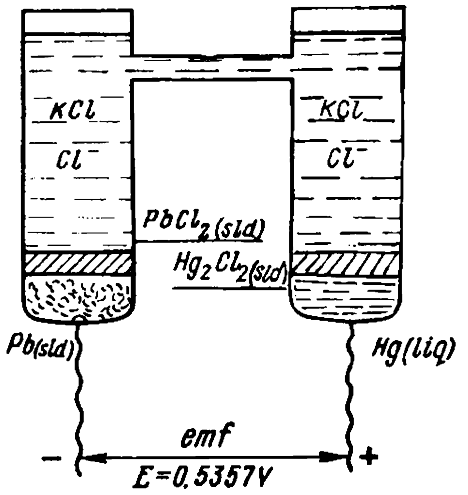

Fig. 5.9. Schematic of a galvanic cell based on reaction (5.68).

Let us consider, as an example, the reaction

$$\mathrm{Pb(sld)} + \mathrm{Hg_2Cl_2(sld)} \rightleftharpoons \mathrm{PbCl_2(sld)} + 2\mathrm{Hg(liq)} \tag{5.68}$$

The heat effect of this reaction can be determined under the conditions of complete nonequilibrium and absence of all kinds of work, except for the work of expansion, i.e., the enthalpy of the reaction $\Delta H = -22{,}430$ cal/mole. In order to measure the useful work, we construct a galvanic cell (Fig. 5.9) based on reaction (5.68). It consists of two half-cells. In the first (on the left in the figure) there is a lead electrode at the bottom of the vessel, covered by a layer of the solid salt $PbCl_2$. At the bottom of the second vessel there is a pool of mercury (the mercury electrode) covered with a layer of solid calomel. The two vessels and the salt bridge are filled with a solution of potassium chloride, which is an auxiliary medium that supplies chloride ions and provides conduction. Experiment shows that the lead in such a system is charged negatively with respect to mercury. Here the cathode is the site of the formation of lead chloride:

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* The condition of constant pressure will be observed if the separate vessels mentioned contain very large amounts of the substances involved, so that the removal of small amounts (ν_i moles) from the vessels will not change the initial pressures significantly.

$$Pb(sld)+2Cl^- = PbCl_2+2e^- \tag{5.69}$$

and the electrons e^- impart a negative charge to the lead electrode. The anode is, on the contrary, the site on which calomel is decomposed:

$$Hg_2Cl_2+2e^- = 2Hg(liq)+2Cl^- \tag{5.70}$$

The mercury electrode which loses electrons becomes positively charged. On the whole, combining the two half-reactions (5.69) and (5.70) gives the net reaction (or the cell reaction) (5.68). Thus, an electromotive force is created in the system which can be measured by the compensation method described in Chapter 2, Sec. 2.9. At 25°C (298.15°K) the electromotive force $E = 0.5357$ volt. The net reaction (5.68) corresponds to the conversion of 2 g-eq of ions and the transport of two faradays of charge. Hence, the maximum useful work of the reaction can be found from the relation

$$W'_T = 2EF = \frac{2\times 0.5357\times 96{,}484.6}{4.1840} = 24{,}706 \text{ cal/mole} \tag{5.71}$$

In other words, reaction (5.68) is accompanied by a loss in the Gibbs free energy since

$$\Delta G_{298} = -24{,}706 \text{ cal/mole} \tag{5.72}$$

The negative value of ΔG_T points to the possibility of a spontaneous reaction.

In connection with the example given above it is interesting to compare the values of ΔG_T and ΔH_T and to consider the important term "chemical affinity". Chemists use this term to describe the factors (or forces as one might say) under the influence of which substances enter into chemical reactions. At present this task is solved, as is usually said, on a molecular level by methods of quantum mechanics. In thermodynamics, which is not concerned with the interactions between individual molecules, one had to find a certain macroscopic measure of the action of chemical forces which could be estimated from phenomena that occur in the system as a whole. The original viewpoint put forward by Thomsen (1853) and formulated in a more explicit form by Berthelot (1867) suggested that the heat effect of reaction be taken as a measure of chemical affinity. Berthelot worked out the following formulation: *Any chemical change effected without the energy from outside tends to produce a body or a system of bodies, this being accompanied by the evolution of a maximum amount of heat.* This proposition is known as the Berthelot-Thomsen principle. This principle, however, cannot be completely valid since it denies the possibility of the spontaneous occurrence of endothermic reactions.

The correct viewpoint which was first advanced by Gibbs (1878) and later by Helmholtz (1884) and van't Hoff (1885) suggested that chemical affinity, i.e., forces that make substances enter into chemical combination, be estimated from the amount of work that these forces are able to perform. Here one must speak of the work done by the system under equilibrium conditions, i.e., the maximum work. Subsequent detailing showed that under the conditions of constant temperature and volume the *net maximum work* that the reacting system can perform, i.e., $W_{T,\mathrm{max}}$, should be taken as a measure of chemical affinity. But if a chemical reaction is carried out at constant temperature and pressure, the measure of chemical affinity must be the maximum useful work $W'_{T,\mathrm{max}}$.

In modern thermodynamics, one speaks of the maximum work of a reaction more and more seldom. The point is evidently that this work is rarely measured in practice. These measurements are relatively easily made only for reactions that can be used to construct a galvanic cell, say, reaction (5.69). In the majority of cases, however, what one is speaking about is not the work itself but the possibility of the work being done under equilibrium conditions of a reaction. In fact, the reaction is carried out under nonequilibrium conditions (for example, the formation of ammonium in the synthesis column) and no work is performed. In connection with what has been said, in thermodynamics use is made of relations (4.12) and (4.28), i. e.,

$$W_{T,v_{\mathrm{max}}} = F_1 - F_2 = -\Delta F_{T,v} \text{ and } W'_{T,p_{\mathrm{max}}} = G_1 - G_2 = -\Delta G_{T,p} \tag{5.73}$$

and the quantities equivalent to the maximum works $W_{T,v_{\mathrm{max}}}$ and $W'_{T,p_{\mathrm{max}}}$ are used as a measure of the affinity, namely, the loss in the Helmholtz free energy $-\Delta F_{T,v}$ (for T = const and v = const) and the loss in the Gibbs free energy $-\Delta G_{T,p}$ (for T = const and p = const). Changes in the thermodynamic properties F and G do not depend on the method used to carry out a process, in particular, on whether it is an equilibrium process or not, and are governed only by the initial and final states of the system. It is also important that the values of $\Delta F_{T,v}$ and $\Delta G_{T,p}$ for reactions can also be determined independently of the work.

The indicated characteristics of the chemical affinity are integral and are calculated per one equivalent of chemical reaction ($\Delta\xi = 1$) provided that all the properties of the reactants are constant, primarily the values of G_i. De Donder (1922) suggested that the chemical affinity A be defined as

$$A = -\left(\frac{\partial x}{\partial \xi}\right)_{y,z} \tag{5.74}$$

where x is one of the characteristic functions (F, G, U, H); y and z are the independently varying properties of the system, for which

x is a characteristic function. Thus,

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -\left(\frac{\partial F}{\partial \xi}\right)_{T,v} = -\left(\frac{\partial H}{\partial \xi}\right)_{S,p} = -\left(\frac{\partial U}{\partial \xi}\right)_{S,v} \qquad (5.75)$$

It must be clear that in a general case the finite changes in $\Delta G_{T,p}$ and $\Delta F_{T,v}$ in Eq. (5.73) are not equal to the corresponding derivatives in Eq. (5.75) and are obtained from the latter provided that the affinity is independent of the chemical variable, which is generally incorrect. It is for this reason that at the beginning of this section we emphasized that the reactants are placed in separate vessels under constant conditions. In another, more real case involving a very large amount of a reaction mixture containing all the reactants, one equivalent of reaction ($\Delta\xi = 1$) does not cause noticeable changes in the composition and, hence, in the affinity A, which in this case coincides with the integral affinity (5.73).

Let us now return to reaction (5.68) and compare the values of ΔG, ΔH and the heat of an equilibrium process. We make use of Eq. (5.35):

$$\Delta G_T = \Delta H_T - T\Delta S_T \qquad (5.76)$$

which we shall call the Gibbs-Helmholtz equation. For reaction (5.68) $\Delta H_T = -22{,}430$ and $\Delta G_T = -24{,}706$ cal/mole. Hence,

$$T\Delta S_T = -22{,}430 + 24{,}706 = 2276 \text{ cal/mole} = Q_{\text{eq}}$$

This relation expresses a very interesting result. The quantity $T\Delta S$ is, according to the second law of thermodynamics [relation (3.9*b*)], the heat of an equilibrium process, Q_{eq}. Reaction (5.68) is exothermic, i.e., it proceeds with the evolution of heat ($\Delta H_T = -22{,}430$). This heat effect, which is determined under the conditions of an entirely nonequilibrium process, i.e., in the absence of all kinds of work, except the expansion work (see Sec. 2.6). But when the reaction is carried out under equilibrium conditions and maximum work is done, the heat is absorbed rather than evolved. And this heat absorbed from the surroundings is converted into work. As a result, the maximum useful work performed by reaction (5.68) is greater than the heat effect in absolute value. The quantities ΔH_T and $T\Delta S_T$ do not differ in sign in all cases, but nevertheless the example given shows possible substantial differences in the evaluation of the "integral affinity" from the heat effect and maximum work. From relation (5.76) we also see under what conditions the Berthelot principle can be valid—evidently when the entropy term $T\Delta S$ is relatively small. This may occur with small changes in the entropy in the reaction, for example, when it occurs in the condensed phase, i.e., when only solid or liquid reactants participate in the reaction, or at low temperatures. The predominance of the heat effect over the entropy term can also be observed in reactions involving gases (see the data presented in Table 5.2). Equation (5.76) was called here the Gibbs-Helmholtz equation. In addition, we can write, on the basis of Eq. (4.4), the following relation:

$$\Delta F_T = \Delta U_T - T\Delta S_T \tag{5.77}$$

which holds at constant temperature and volume; this equation may also be called the Gibbs-Helmholtz equation.

In thermodynamics, however, somewhat different relations are known as the Gibbs-Helmholtz equations, those following directly from Eqs. (5.76) and (5.77). As is known, the derivatives $(\partial G/\partial T)_p = -S$ and $(\partial F/\partial T)_v = -S$ [Eqs. (4.43) and (4.46)] and, therefore, differentiating the difference $G_2 - G_1 = \Delta G$ with respect to temperature, we can write:

$$\left(\frac{\partial G_2}{\partial T}\right)_p - \left(\frac{\partial G_1}{\partial T}\right)_p = \left(\frac{\partial \Delta G}{\partial T}\right)_p = -S_2 - S_1 = -\Delta S \tag{5.78}$$

or, in an analogous way,

$$\left(\frac{\partial \Delta F}{\partial T}\right)_v = -\Delta S \tag{5.79}$$

Therefore, first, instead of relations (5.76) and (5.77) we can write the following relations:

$$\Delta G_T = \Delta H_T + T\left(\frac{\partial \Delta G}{\partial T}\right)_p \tag{5.80}$$

and

$$\Delta F_T = \Delta U_T + T\left(\frac{\partial \Delta F}{\partial T}\right)_v \tag{5.81}$$

Second, using the relation between ΔG_T and ΔF_T and the maximum useful work and the maximum net work, we can rewrite Eqs. (5.80) and (5.81) as follows:

$$W'_{T,\max} = -\Delta H_T + T\frac{\partial W'_{T,\max}}{\partial T} \tag{5.82}$$

and

$$W_{T,\max} = -\Delta U_T + T\frac{\partial W_{T,\max}}{\partial T} \tag{5.83}$$

As has already been said, the maximum work is measured in practice with the aid of a galvanic cell from the relation $W'_T = zEF$, where z is the number of gram-equivalents of the ions being converted; E is the electromotive force of the cell; F is Faraday's number equal to 96,484.6 C/mole. So, we can rewrite Eq. (5.82), converting joules into calories ($F = 96{,}484.6/4.1840 = 23{,}060.4$ cal/V·mole):

$$E = -\frac{\Delta H_T}{z\,23{,}060.4} + T\left(\frac{\partial E}{\partial T}\right)_p \tag{5.84}$$

Relations (5.82), (5.83) and (5.84) are usually called the Gibbs-Helmholtz equations. On the basis of Eq. (5.84) we can say that the electromotive force of a galvanic cell can be found from the heat effect of reaction by means of Berthelot's principle (and not from the maximum work) if $\partial E/\partial T = 0$, i.e., if the electromotive force of the cell is independent of temperature. Berthelot's principle was historically verified precisely by the equality $E = -\Delta H_T/z \cdot 23{,}062$ for a randomly chosen Daniell cell based on the reaction

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu} \tag{5.85}$$

for which $\Delta S \approx 0$ and, hence, $\partial E/\partial T$ is also approximately equal to zero.

5.4. Standard Gibbs Free-Energy Change

In Sec. 2.6 we introduced the concept of the standard states of substances and of the standard heat effects of reactions, primarily the concept of the standard enthalpies of a reaction, ΔH°_T. Suppose now that all the participants in reaction (5.65) are in standard states, i.e., the gaseous substances are in separate vessels at a pressure of 1 atm and in the form of ideal gases, and the solid and liquid substances are in their most stable state, also at a pressure of 1 atm. If the reactants in their standard states form products which are also in their standard states, relation (5.66) can be rewritten in the form:

$$\nu'_1 \underline{G}^{\circ\prime}_1 + \nu'_2 \underline{G}^{\circ\prime\prime}_2 + \ldots - \nu_1 \underline{G}^\circ_1 - \nu_2 \underline{G}^\circ_2 - \ldots = \Delta G^\circ_T \tag{5.86}$$

where $\underline{G}^\circ_i$ are the molar standard Gibbs energies of substances B_i and the quantity ΔG°_T is the most important thermodynamic characteristic of the reaction—the standard Gibbs free-energy change or simply the *standard Gibbs energy* (or the *standard free energy of reaction*). The superscript zero in ΔG° refers to pure components. The standard Gibbs energy of a reaction depends on temperature and, therefore, for the sake of definiteness and for the purposes of possible combinations for various reactions they are determined primarily for 25°C or 298.15°K and are designated as ΔG°_{298}. It is this symbol which is used in thermodynamic tables for standard Gibbs energies of reactions, say, the formation of compounds from simple substances.

The standard Gibbs energies of reactions are usually found by means of the Gibbs-Helmholtz equation in the form (5.76), using the standard heats and standard entropies of the substances (the participants in the reaction). For the temperature 25°C Eq. (5.76) assumes the form

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - 298.15\ \Delta S^\circ_{298} \tag{5.87}$$

As an example, we shall calculate ΔG°_{298} for the conversion of methane into acetylene:

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \tag{5.88}$$

In tables of thermodynamic quantities we find, first, the standard enthalpies of the formation of the reactants, ΔH°_{298}, and then, their standard entropies. These quantities have the following values:

Reactant	Standard enthalpy of formation ΔH°_{298}, cal/mole	Standard entropy ΔS°_{298}, cal/deg·mole	Heat capacity* C°_{298}, cal/deg × × mole
CH_4	—17,889	44.50	8.54
C_2H_2	54,194	48.00	10.50
H_2	0	31.21	6.89

From the data of the second column we find (according to Hess's law) the standard enthalpy of reaction (5.88):

$$\Delta H^{\circ}_{298} = 54{,}194 + 2 \times 17{,}889 = 89{,}972 \text{ cal/mole } C_2H_2 \tag{5.89}$$

and then its standard entropy:

$$\Delta S^{\circ}_{298} = 48.00 + 3 \times 31.21 - 2 \times 44.50 = 52.63 \text{ eu} \tag{5.90}$$

Finally, using Eq. (5.87), we find:

$$\Delta G^{\circ}_{298} = 89{,}972 - 298.15 \times 52.63 = 74{,}280 \text{ cal/mole } C_2H_2 \tag{5.91}$$

Thus, the formation of one mole of acetylene and three moles of hydrogen from two moles of methane (provided that all the reactants are in their standard states) is accompanied by a large increase in the Gibbs free energy of the system. This means that the formation of acetylene (in standard states) is impossible** and, moreover, that it is thermodynamically unstable towards methane and hydrogen since the reaction, which is the reverse of process (5.91), would have occurred with a loss in the Gibbs energy equal to —74,280 cal/mole of C_2H_2. It is these thermodynamic properties of acetylene that account for its ability to decompose with an explosion, especially at somewhat higher pressures.

The Gibbs energies of reactions, including the standard Gibbs energies, can be calculated on the basis of the generalized Hess law. Since we are speaking of a property of the system, its change is independent of the path taken by the process and, hence, we can combine ΔG for various reactions, just in the same way as the heat effects are combined on the basis of Hess's law. Thus, in tables of thermodynamic quantities we can find the standard Gibbs energies of formation of acetylene and methane from simple substances:

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* Heat capacity values will be used at a later time in calculations of the dependence of ΔG on temperature.

** It will be shown later (see Sec. 5.11) that acetylene can also be formed in a small (negligibly small) concentration in a mixture of methane and hydrogen even at 298°K.

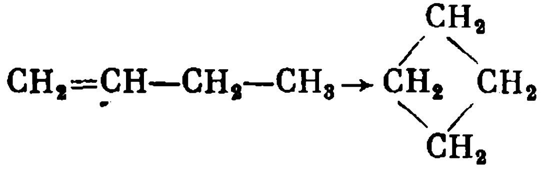
1. $2C \text{ (graphite)} + H_2 = C_2H_2 \quad \Delta G^\circ_{298} = 50{,}000$ cal/mole
2. $C \text{ (graphite)} + 2H_2 = CH_4 \quad \Delta G^\circ_{298} = -12{,}140$ cal/mole

First, note the possible spontaneous formation of methane from simple substances under standard conditions—reaction (2) is accompanied by a loss in the Gibbs energy. Second, subtracting the doubled second reaction from reaction (1), we obtain for the process of formation of acetylene from methane (5.88):

$$\Delta G^\circ_{298} = 50{,}000 + 2 \times 12{,}140 = 74{,}280 \text{ cal/mole } C_2H_2 \qquad (5.92)$$

that is, a value which coincides with that found earlier (5.91).

Of some historical interest is the reaction of isomerization of butene (butylene) to cyclobutane:



(5.93)

The heat effect of this reaction ΔH°_{298} is equal to 6400 cal/mole, i.e., the reaction is endothermic and, moreover, it is accompanied by a loss in the entropy:

$$\Delta S^\circ_{298} = S^\circ_{298} \text{ (cyclobutane)} - S^\circ_{298 \text{ (butene)}} = -9.61 \text{ eu}$$

Hence, the standard Gibbs energy of reaction (5.93) is

$$\Delta G^\circ_{298} = 6400 + 9.61 \times 298.15 = 9960 \text{ cal/mole}$$

In other words, the isomerization of butene under standard conditions proceeds with an increase in the Gibbs energy, i.e., it is characterized by a negative affinity; it is therefore not surprising that the attempts of organic chemists to accomplish this reaction have failed.

Using tables of thermodynamic quantities, Hess's law and Eq. (5.87), let us draw up the thermodynamic characteristics of some simple reactions involving gases (Table 5.2). The four reactions chosen have something in common—in all these reactions, from two moles of gas there are produced three moles of gaseous substances. In view

TABLE 5.2. The Thermodynamic Characteristics of Selected Simple Reactions Involving Gases

Reaction	ΔH°_{298}, kcal/mole	ΔS°_{298}, cal/deg·mole	ΔG°_{298}, kcal/mole	No. of reaction
$2CO_2 = 2CO + O_2$	135.3	41.5	122.9	(5.94)
$2N_2O = 2N_2 + O_2$	−39.0	35.4	−49.5	(5.95)
$2NO_2 = 2NO + O_2$	27.0	34.7	16.7	(5.96)
$2NO_2 = N_2 + 2O_2$	−16.2	28.8	−24.8	(5.97)

TABLE 5.3. **The Thermodynamic Characteristics of Some Substances: the Standard Heats, Entropies and Gibbs Free Energies of Reactions of Their Formation from Simple Substances***

Substance	ΔH°_{298}, kcal/mole	S°_{298}, kcal/deg·mole	ΔG°_{298}, kcal/mole
Ag (g)	69.12	41.322	52.84
AgCl (g)	23.23	58.5	16.79
AgCl (sld)	−30.36	22.97	−26.22
Al (g)	75.00	39.303	65.3
$AlCl_3$ (sld)	−166.2	25.64	−152.2
B (g)	97.2	36.649	86.7
BCl_3 (g)	−94.5	69.29	−90.9
B_2H_6 (g)	7.5	55.66	19.8
Ba (g)	−41.96	40.699	34.60
$BaCl_2$ (sld)	−205.56	30	−193.8
C (g)	171.698	37.761	160.845
C (diamond)	0.4532	0.5829	0.6850
C (graphite)	0.000	1.3909	0.000
CO (g)	−26.416	47.216	−32.808
CO_2 (g)	−94.052	51.071	−94.260
H (g)	52.089	27.3927	48.575
H_2 (g)	0.000	31.208	0.000
D_2 (g)	0.000	34.602	0.000
HD (g)	0.037	34.341	−0.391
H_2O (g)	−57.7979	45.106	−54.6357
H_2O (liq)	−68.3164	16.716	−56.6902
H_2O_2 (liq)	−44.88	—	—
N (g)	85.565	36.6147	81.471
NO (g)	21.600	50.339	20.719
O (g)	59.159	38.4689	54.994
O_3 (g)	34.5	56.8	39.06
OH (g)	10.06	43.888	8.93
CH_4 (g)	−17.889	44.50	−12.140
C_2H_2 (g)	54.194	47.997	50.000
C_2H_6 (g)	−20.236	54.85	−7.860
C_6H_6 (g)	19.820	64.34	30.989
cyclo-C_6H_{12}	−29.43	71.28	7.59

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* *Chemist's Handbook*, volumes I and II, Goskhimizdat, Moscow, 1963.

of this, as can be seen, the entropy changes are positive in all cases and do not differ very strongly because the increments in the entropy in all four reactions are associated with the appearance of a mole of substance in the most random gaseous state.

But the heat effects differ greatly—from the endothermic process of dissociation of CO_2 (+135.3 kcal/mole) to the exothermic decomposition of nitrous oxide into nitrogen and oxygen. Comparison of the values of ΔG with the heat effects shows that the latter determine the sign and magnitude of ΔG for these reactions and, hence, the thermodynamically probable direction of the reaction. In this connection, without rejecting the earlier mentioned criticism of Berthelot's principle, it should be noted that there are many cases where a generally incorrect principle has come to be true. For instance, the high positive values of ΔH for reactions (5.94) and (5.96) also determine the positive change in the Gibbs energy. Hence, under standard conditions reverse reactions can occur spontaneously. The converse is true for nitrous oxide. Here the negative value of ΔH leads to a negative value of ΔG and this makes one consider N_2O to be an unstable substance under ordinary conditions. The fact that it can be used in the laboratory and in medical practice is accounted for by kinetic factors, i.e., by the very low rate of decomposition of nitrous oxide, which in the absence of catalysts renders it practically stable.

It is interesting to compare the last two reactions, (5.96) and (5.97) (see Table 5.2). Their comparison allows the two processes of decomposition of nitrogen dioxide to be compared from a thermodynamic standpoint. As is found, NO_2 must not decompose under standard conditions into nitrogen oxide and oxygen, but the reverse reaction is spontaneous. But the same nitrogen dioxide is unstable and can be decomposed into simple substances, i.e., nitrogen and oxygen.*

Table 5.3 lists the main thermodynamic characteristics of some substances.

5.5. Temperature Dependence of Gibbs Free Energy

As has been said above, the main thermodynamic characteristic of a chemical reaction ΔG_T depends rather strongly on temperature. This dependence is established by various methods; mention should be made, first of all, of the analytical method of derivation of the function $\Delta G_T = f(T)$ and also of the analytical calculation of ΔG_T for ideal gases at various temperatures by the methods of statistical thermodynamics (see Chapter 6). Let us consider the first method. We shall proceed from the known Gibbs-Helmholtz equation (5.76); we rewrite it, remembering the constancy of pressure and replacing the partial derivative by an ordinary one:

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* Attempts have recently been made to solve, on the basis of the above-given thermodynamic analysis of reactions (5.96) and (5.70), the problem of purification of automobile exhausts from the nitrogen oxides that pollute the air we breathe. It is suggested that nitric oxide be converted to nitrogen dioxide by the reaction which is the reverse of (5.96) and NO_2 be then decomposed catalytically into nitrogen and oxygen by reaction (5.97).

$$\Delta G_T = \Delta H_T + T\frac{d\Delta G}{dT} \tag{5.98}$$

Rearranging the last expression and dividing it by T^2, we have

$$\frac{Td\Delta G - \Delta G_T dT}{T^2} = -\frac{\Delta H_T}{T^2}dT \tag{5.99}$$

The left side of Eq. (5.99) is the differential of the fraction $\Delta G/T$ and therefore

$$d\left(\frac{\Delta G_T}{T}\right) = -\frac{\Delta H_T}{T^2}dT \tag{5.100}$$

Thus, we have just obtained the equation which forms the basis for the analytical calculation of the dependence of ΔG_T on temperature.

Before we consider the various methods of using Eq. (5.100) let us agree that it will be applied predominantly to standard conditions; to do this, it will suffice to place the superscript zero on the quantities ΔG_T and ΔH_T, i.e.,

$$d\left(\frac{\Delta G^\circ}{T^2}\right) = -\frac{\Delta H_T^\circ}{T^2}dT \tag{5.101}$$

Further, we take the indefinite integral of relation (5.101):

$$\Delta G_T^\circ = -T\int\frac{\Delta H_T^\circ}{T^2}dT + JT \tag{5.102}$$

where J is the integration constant which must be calculated in each particular case; and in order to calculate the integral on the right-hand side, use must be made of the dependence of the heat effect on temperature given by Kirchhoff's equation (2.119). The following relation is obtained in a general form:

$$\Delta G_T^\circ = -T\int\frac{\Delta H_J + \int\Delta C_p\,dT}{T^2}dT + JT \tag{5.103}$$

Let us now recall that the use of Kirchhoff's equation was considered in three approximations:

1. The heat capacities of reactants and products are equal, i.e., $\Delta C_p = 0$ and $\Delta H_T^\circ = \Delta H_J = \text{const}$.
2. The heat capacities of reactants and products are different but their difference is constant: $\Delta C_p = \text{const}$.
3. The heat capacities of reactants depend on temperature.

Let us consider formula (5.103) in the same three approximations. In the first approximation, which is the crudest, we have:

$$\Delta G_T^{\bullet} = \Delta H + JT \qquad (5.104)$$

Here we have omitted the superscript and subscript for ΔH since they are meaningless in this approximation. Despite the approximate character, formula (5.104) can be used not in a very wide temperature range and for approximate calculations. We shall make use of it at a later time for the integration of the van't Hoff isobar; at this point we confine ourselves to the consideration of a graph (Fig 5.10) showing the dependence of the Gibbs free energy on the temperature of dissociation of tetramethylammonium hydrofluoride:

$$(CH_3)_4NFHF(sld) \rightleftharpoons (CH_3)_4NF(sld) + HF \qquad (5.105)$$

As can be seen from Fig. 5.10, in this case the linear relationship (5.104) is satisfactorily fulfilled. Note that formula (5.104) can also be obtained directly from Eq. (5.76) $\Delta G = \Delta H - T\Delta S$, assuming that, apart from the constancy of the heat effect of the reaction, the entropy change is independent of temperature. Thus, in the approximation under consideration the integration constant

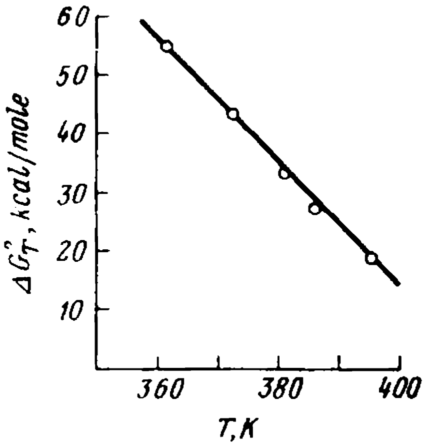

Fig. 5.10. The change in $\Delta G_T^{\bullet}$ with temperature for the dissociation reaction (5.105) satisfies the linear dependence (5.104).

$$J = -\Delta S \qquad (5.106)$$

that is, it is equal to the entropy of the reaction. Formula (5.104) together with Eq. (5.106) is useful in another respect as well, namely it indicates that the change in the entropy term $T\Delta S$ is mainly responsible for the change of ΔG of the reaction with temperature. In other words, the Gibbs energy of the reaction depends on temperature the more strongly the more pronounced is the change of the entropy of the system during the course of the reaction, i.e., the more pronounced is the change in the randomness of its molecular state.* Table 5.4 presents data showing the change in ΔG_T for some reactions over the temperature range 298-596°K. As can be seen, the dependence $\Delta G = f(T)$ is rather strong, though it is not characteristic of ΔH and ΔS taken separately.

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* For an interpretation of the entropy as the measure of the disorder of the molecular state of the system, see Chapter 6 (Sec. 6.1).

TABLE 5.4. **An Illustration of the Temperature Dependence of the Gibbs Free Energy of Reactions**

Reactions involving gases	ΔG°_{298}, kcal/mole	ΔG°_{598}, kcal/mole
$NO\ (g) + \frac{1}{2} O_2\ (g) = NO_2\ (g)$	− 8.33	−2.97
$CO\ (g) + \frac{1}{2} O_2\ (g) = CO_2\ (g)$	−61.4	−55.1
$C_2H_4\ (g) + H_2\ (g) = C_2H_6\ (g)$	−24.1	−15.2
Reactions involving solids:		
$CaCO_3\ (sld) = CaO\ (sld) + CO_2\ (g)$	+31.2	+19.8
$C\ (graphite) + \frac{1}{2} O_2\ (g) = CO\ (g)$	−32.8	−39 4

Let us now turn our attention to the second approximation in which the difference of the heat capacities is assumed to be constant. If ΔC_p = const, then the integration of Eq. (5.103) leads to the following result:

$$\Delta G^\circ_T = \Delta H_J - \Delta C_p T \ln T + JT \tag{5.107}$$

Or, converting to decimal logarithms,

$$\Delta G^\circ_T = \Delta H_J - 2.303\ \Delta C_p T \log T + JT \tag{5.108}$$

As compared with formula (5.104), this formula describes more precisely the dependence $\Delta G = f(T)$ and it can be used for a wider temperature range.

Let us now return to the reaction of conversion of methane to acetylene (5.88), for which it has been found that $\Delta G^\circ_{298} = 74{,}280$ cal/mole.

The heat capacities of the reactants for this reaction were given on page 157; using the values given, we find ΔC°_p:

$$\Delta C^\circ_p = 10.5 + 3 \times 6.89 - 2 \times 8.54 = 14.09 \text{ cal/deg·mole}$$

Further, writing Kirchhoff's equation in the second approximation

$$\Delta H^\circ_T = \Delta H_J + \Delta C^\circ_p T$$

we find the constant ΔH_J if, as follows from Eq. (5.89),

$$\Delta H^\circ_{298} = 89{,}972$$

$$\Delta H_J = \Delta H^\circ_{298} - \Delta C^\circ_p\, 298.15 = 89{,}972 - 14.09 \times 298.15 = \\ = 85{,}771 \text{ cal/mole} \tag{5.109}$$

Now we can rewrite the formula for ΔG°_T (5.108) in the form:

$$\Delta G^\circ_T = 85{,}771 - 14.09\ T \ln T + JT$$

Here the integration constant J remains to be unknown. We determine it by using the known value of $\Delta G^\circ_{298} = 74{,}280$ cal/mole:

$$J = \frac{\Delta G^\circ_{298} - \Delta H_J}{298.15} + \Delta C^\circ_p \ln 298.15 = \frac{74{,}280 - 85{,}771}{298.15} + $$
$$+ 14.09 \times 2.303 \log 298.15 = 41.750$$

We can now write the final formula of the second approximation:

$$\Delta G^\circ_T = 85{,}771 - 14.09 \times 2.303\, T \log T +$$
$$+ 41.750\, T \text{ cal/mole } C_2H_2 \qquad (5.110)$$

Table 5.5 lists values of ΔG°_T for a number of temperatures. Thus, the standard Gibbs free energy of the reaction

$$2CH_4 = C_2H_2 + 3H_2$$

changes its sign with increasing temperature and at 1500°K the reaction under standard conditions becomes spontaneous. This calculation made over a rather wide temperature range cannot claim for a high accuracy but it nevertheless gives a correct picture of the general character of the dependence of the Gibbs free energy of reaction (5.88) on temperature. It is just at temperatures above 1500°K that acetylene can be prepared from methane. In technological methods the required high temperature is attained either with the aid of a powerful electric arc (the electrocracking method) or by burning part of methane (oxidative conversion).

TABLE 5.5. The Values of the Standard Gibbs Free Energy of Reaction (5.88) for Various Temperatures

T, °K	ΔG°_T, kcal/mole		
	Second approximation, formula (5.110)	Third approximation, formula (5.115)	Calculation from JANAF tables*
298.15	74.280	74.280	74.283
500	62.857	62.894	62.871
750	47.113	47.489	47.380
1000	30.174	31.411	31.272
1250	12.344	15.100	14.903
1500	—6.195	—1.194	—1.541
1750	—25.325	—17.294	—17.986
2000	—44.959	—33.104	—34.412

* See the references at the end of the book.

When it is necessary to obtain a more precise dependence by means of the third approximation, recourse is made to the various formulas that describe the temperature dependence of heat capacity (such formulas have already been discussed in Chapter 2 in connection with the use of Kirchhoff's formula). If, as is often the case, the heat capacities of the participants in the reaction are expressed in terms of empirical power series, say

$$C_p^\circ = a + bT + cT^2 + \ldots$$

then ΔC_p° is also given by a power series:

$$\Delta C_p^\circ = \Delta a + \Delta bT + \Delta cT^2 + \ldots$$

Substituting this value into the integral of Eq. (5.103), we obtain the expression

$$\Delta G_T^\circ = \Delta H_J - \Delta aT \ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{6}\Delta cT^3 - \ldots + JT \qquad (5.111)$$

which Lewis and Randall call the general free-energy equation*. Here the quantities ΔH_J and J, which are constant for a given reaction, must be determined through the use of Kirchhoff's equation of the third approximation (2.134) and directly from formula (5.111). In other words, these constants will differ from the analogous constants in formula (5.107). But if we make use of a different function of heat capacity, namely (2.131), then the following expression is obtained for the heat effect in accordance with Kirchhoff's equation:

$$\Delta H_T^\circ = \Delta H_J + \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 - \Delta c'T^{-1} \qquad (5.112)$$

and the equation of the third approximation for the Gibbs free energy assumes a form which differs from Eq. (5.111) by an additional term:

$$\Delta G_T^\circ = \Delta H_J - \Delta aT \ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{6}\Delta cT^3 - \frac{1}{2}\Delta c'T^{-1} + JT \qquad (5.113)$$

Let us calculate the value of ΔG_T° for the reaction $2CH_4 = C_2H_2 + 3H_2$ from this equation, using the heat capacities of the substances given in Table 2.2, in the functions of which the terms in T^3 are omitted. We assume the following values:

1. for CH_4: $C_p^\circ = 5.65 + 11.44 \times 10^{-3}\ T - 0.46 \times 10^5 T^{-2}$ cal/deg·mole
2. for H_2: $C_p^\circ = 6.52 + 0.78 \times 10^{-3}\ T + 0.12 \times 10^5\ T^{-2}$ cal/deg·mole
3. for C_2H_2: $C_p^\circ = 12.13 + 3.84 \times 10^{-3}\ T - 2.46 \times 10^5\ T^{-2}$ cal/deg·mole

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* In their book Lewis and Randall use ΔF for the Gibbs free-energy change.

We now find:

$$\Delta a = 20.39,\ \Delta b = -16.70 \times 10^{-3} \text{ and } \Delta c' = -1.18 \times 10^{5}$$

and write Kirchhoff's equation (5.112) for 298.15°K:

$$\Delta H^{\circ}_{298} = 89{,}972 = \Delta H_J + 20.39 \times 298.15 - \frac{1}{2} \times 16.70 \times \\ \times 10^{-3}(298.15)^2 + 1.18 \times 10^{5}(298.15)^{-1}$$

From this equation with one unknown we determine the constant

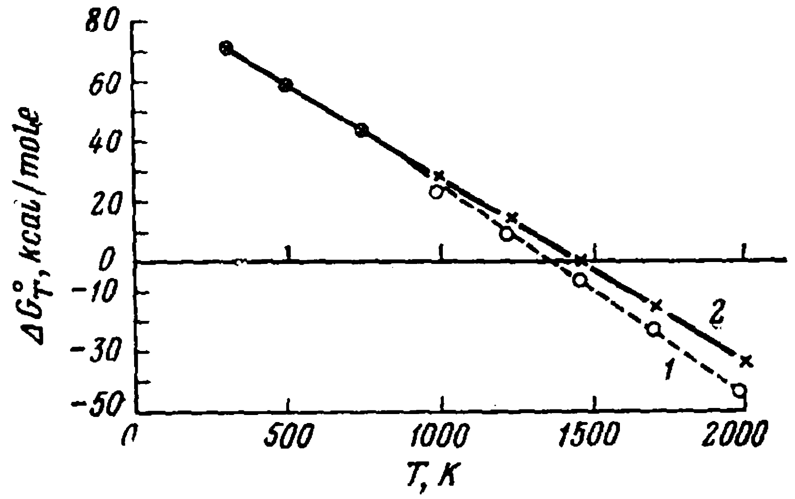

Fig. 5.11. Dependence of the standard Gibbs free energy of the reaction $2CH_4 = C_2H_2 + 3H_2$ on temperature:
1—second approximation ΔC_p = const, formula (5.110); 2—third approximation $\Delta C_p = f(T)$, formula (5.115).

$\Delta H_J = 84{,}239$. Then we write formula (5.113) with known values of the constants:

$$\Delta G^{\circ}_{298} = 74{,}280 = 84{,}239 - 20.39 \times 2.303 \times 298.15 \log 298.15 + \\ + 8.35 \times 10^{-3}(298.15)^2 + 0.59 \times 10^{-5}(298.15)^{-1} + J\,298.15 \tag{5.114}$$

and calculate $J = 79.637$. Now the third-approximation formula takes the following final form:

$$\Delta G^{\circ}_{T} = 84{,}239 - 46.958\,T \log T + 8.35 \times 10^{-3}\,T^2 + \\ + 0.59 \times 10^{5}\,T^{-1} + 79.637\,T \tag{5.115}$$

The values of ΔG°_{T} calculated from this formula for the same temperatures as before are given in Table 5.5. From the data obtained it is seen that there is a considerable difference between the third approximation and the incomparably simpler, second approximation at very high temperatures, i.e., 1500, 1750 and 2000°K, when it becomes possible to accomplish the reaction. Thus, in this particular case the second approximation fails to indicate the possible yields of acetylene at high temperatures. As for moderate temperatures the second approximation gives satisfactory results.

Figure 5.11 presents the results of calculations in the form of the dependence $\Delta G_T^\circ = f(T)$. As can be seen, the two graphs depart from a straight line, but it is curious that in this case the dependence of the more accurate, third approximation is closer to linear.

We shall now consider one more variant of the use of Eq. (5.101), which, first, is integrated within the range of variation of temperature from 298.15 to T:

$$\frac{\Delta G_T^\circ}{T} - \frac{\Delta G_{298}^\circ}{298.15} = -\int_{298.15}^{T} \frac{\Delta H_T^\circ}{T^2}\, dT = -\int_{298.15}^{T} \frac{\Delta H_{298}^\circ + \int_{298.15}^{T} \Delta C_p\, dT}{T^2}\, dT =$$

$$= -\int_{298.15}^{T} \frac{\Delta H_{298}^\circ}{T^2}\, dT - \int_{298.15}^{T} \frac{1}{T^2}\left(\int_{298.15}^{T} \Delta C_p^\circ\, dT\right) dT =$$

$$= \frac{\Delta H_{298.15}^\circ}{T} - \frac{\Delta H_{298.15}^\circ}{298.15} - \int_{298.15}^{T} \frac{dT}{T^2} \int_{298.15}^{T} (\Delta a + \Delta b T + \Delta c T^2 + \Delta c' T^{-2})\, dT$$

Here the power series (2.131) are used on the right-hand side upon integration. Second, the following equality is also used:

$$\Delta G_{298.15}^\circ = \Delta H_{298.15}^\circ - 298.15\, \Delta S_{298.15}^\circ$$

and the following result is obtained:

$$\frac{\Delta G_T^\circ}{T} = \frac{\Delta H_{298}^\circ}{T} - \Delta S_{298}^\circ - \Delta a \int_{298.15}^{T} \frac{dT}{T^2} \int_{298.15}^{T} dT -$$

$$- \Delta b \int_{298.15}^{T} \frac{dT}{T^2} \int_{298.15}^{T} T\, dT - \Delta c \int_{298.15}^{T} \frac{dT}{T^2} \int_{298.15}^{T} T^2\, dT -$$

$$- \Delta c' \int_{298.15}^{T} \frac{dT}{T^2} \int_{298.15}^{T} T^{-2}\, dT \qquad (5.116)$$

In the last equality the coefficients Δa, Δb . . . are taken outside the integral signs and the integrals themselves depend only on the upper limit of integration; their values have been calculated and collected in tabular form by Temkin and Shvartsman (see Appendix 3). The integrals of Eq. (5.116) are called *a priori* coefficients and are designated by the symbols M_0, M_1, M_2, . . ., M_{-2}; the subscript for M is determined by the exponent in the expansion series of the heat capacity:

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ - T\{\Delta a M_0 + \Delta b M_1 + \Delta c M_2 + \dots + \Delta c' M_{-2}\} \qquad (5.117)$$

In order to calculate ΔG_T° from this formula it will suffice to know the heat effect of the reaction, the standard entropies of the substances at 298.15°K and also the coefficients in the expressions for the heat capacities. The calculations can be considerably facilitated by using the tables of Appendix 3.

The above methods of determining the Gibbs energy described above may be called analytical. However, an ever increasing use is made of methods which call for the compilation and use of tables of thermodynamic properties at various temperatures. In principle, one might collect values of ΔG for reactions at various temperatures. There are, however, very many reactions and it is impossible to draw up tables for them all. Besides, the quantity ΔG varies strongly with temperatures and, therefore, in order to have sufficiently accurate data for any temperature, one would have to tabulate values over narrow temperature ranges.

Two closely related thermodynamic functions have been found to be convenient for tabulation:

$$\Phi = -\frac{G_T^\circ - H_0^\circ}{T} \qquad (5.118)$$

and

$$\Phi' = -\frac{G_T^\circ - H_{298}^\circ}{T} \qquad (5.119)$$

The two functions may be called the *reduced Gibbs energies* of a substance, Φ being the reduced Gibbs energy based on zero enthalpy (H_0°) and Φ' the reduced Gibbs energy based on H_{298}°, i.e., the enthalpy at 298.15°K. It will be shown in Chapter 6 that for gases the function Φ can be calculated directly by the methods of statistical thermodynamics if the molecular energy levels have been determined spectroscopically. For solids the reduced Gibbs energy can be computed, using the third law of thermodynamics, by means of graphical methods or by calculating one of the following double integrals:

$$-\Phi = \frac{G_T^\circ - H_0^\circ}{T} = -\frac{1}{T}\int_0^T dT \int_0^T \frac{C_p^\circ}{T}\, dT \qquad (5.120)$$

and

$$-\Phi = \frac{G_T^\circ - H_0^\circ}{T} = -\int_0^T \frac{dT}{T^2} \int_0^T C_p^\circ\, dT \qquad (5.121)$$

Relation (5.120) results from the integration of the differential $dG = -S\,dT$ (p = const) and expression (5.121) is derived by a method similar to the derivation of Eq. (5.103). One should also take into account the equality

$$S_T^\circ = \frac{H_T^\circ - H_0^\circ}{T} - \frac{G_T^\circ - H_0^\circ}{T} \tag{5.122}$$

Since the first integration in Eq. (5.120) gives the entropy, we can make use of relation (5.122) to determine the enthalpy of substances $H_T^\circ - H_0^\circ$ without calculating the corresponding integral. When Eq. (5.121) is utilized, the first integration also yields $H_T^\circ - H_0^\circ$ and equality (5.122) allows us to find the entropy of the substance, S_T°. In formulas (5.120), (5.121) and (5.122) the symbol H_0° signifies the standard zero enthalpy, i.e., the enthalpy referred to absolute zero. Therefore, in calculating the integrals of Eqs. (5.120) and (5.121) one must make use of the functions $C_p = f(T)$, which retain their values until the region close to absolute zero is reached. At absolute zero, from the definitions it is clear that

$$G_0 = H_0 = U_0 = F_0 \tag{5.123}$$

Let us illustrate the use of the reduced Gibbs energy Φ by the example of the following phase transition:

$$S_{\text{rhomb}} \rightleftharpoons S_{\text{monocl}} \tag{5.124}$$

Table 5.6 lists the calorimetrically determined values of enthalpy and entropy for the two modifications of sulphur and the reduced Gibbs energies calculated from them at the temperatures 240, 298.15, 350 and 368.5°K. This table is a combination of two tables for the two substances. The last column gives the values of the difference:

TABLE 5.6. The Reduced Gibbs Energy for Two Modifications of Sulphur, cal/deg·mole (a combination of two tables for S_{rhomb} and S_{monocl})

T, °K	Rhombic			Monoclinic			$\Delta\Phi$ (5.123)=	ΔG_T°, cal/mole
	$\frac{H_T^\circ - H_0^\circ}{T}$	S_T°	$-\frac{G_T^\circ - H_0^\circ}{T}$	$\frac{H_T^\circ - H_0^\circ}{T}$	S_T°	$-\frac{G_T^\circ - H_0^\circ}{T}$	$= \frac{\Delta G_T^\circ - \Delta H_0^\circ}{T}$	
240	3.12	6.50	3.38	3.21	6.62	3.41	−0.03	+33.3
298.15	3.53	7.62	4.09	3.65	7.82	4.17	−0.08	+16.6
350	3.83	8.51	4.68	3.97	8.74	4.77	−0.09	9.0
368.6	3.93	8.81	4.88	4.08	9.07	4.99	−0.11	0.0
380	—	—	—	—	—	—	—	−3.0

$$\left(\frac{\Delta G_T^\circ - \Delta H_0^\circ}{T}\right) = \Phi_{\text{rhomb}} - \Phi_{\text{monocl}} =$$

$$= \left(\frac{G_T^\circ - H_0^\circ}{T}\right)_{\text{monocl}} - \left(\frac{G_T^\circ - H_0^\circ}{T}\right)_{\text{rhomb}} \tag{5.125}$$

In order to calculate the Gibbs energies of interest, it is necessary to know the heat effect of the reaction at absolute zero, i.e., ΔH_0°. If it is known, then

$$\Delta G_T^\circ = -T\Delta\Phi + \Delta H_0^\circ = T\left(\frac{\Delta G_T^\circ - \Delta H_0^\circ}{T}\right) + \Delta H_0^\circ \tag{5.126}$$

In this particular case the question of the determination of ΔH_0° is solved in a simple way. At the temperature 368.6°K the two modifications of sulphur are at equilibrium (the point of transition) and $\Delta G_{368.6}^\circ \approx 0$. Therefore, from the value of $(\Delta G_T^\circ - \Delta H_0^\circ)/T$ equal to -0.11 at a temperature of 368.6°K it is easy to determine $\Delta H_0^\circ = 0.11 \times 368.6 \approx 40.5$ cal/mole. We can now find ΔG_T° at any other temperature. For example, for 298.15°K

$$\Delta G_{298}^\circ = 298.15\,(-0.08) + 40.5 = 16.6 \text{ cal/mole}$$

that is, at this temperature the rhombic modification is more stable than the monoclinic one.

Thus, the determination of the values of ΔG_T° at various temperatures with the aid of tables containing the functions Φ, if there are such, is significantly facilitated as compared with the analytical calculations of ΔG_T°, especially by means of the third-approximation equations of the type (5.113), which employ complex functions for heat capacities and which are applicable over a wide range of temperatures.

The second function Φ' (5.119) based on H_{298}° is also very useful; its values for various substances are also tabulated. It is obvious that

$$\Phi' = -\frac{G_T^\circ - H_{298}^\circ}{T} = -\frac{H_T^\circ - H_{298}^\circ}{T} + S_T^\circ \tag{5.127}$$

The functions Φ and Φ' are interrelated as follows:

$$\Phi' = \Phi + \frac{H_{298}^\circ - H_0^\circ}{T} \tag{5.128}$$

Combining the tabulated values of the function Φ' for the reactants and products and also the heat effect of the reaction at 298.15°K, we can determine ΔG_T°, i.e.,

$$\Delta G_T^\circ = -T\Delta\Phi' + \Delta H_{298}^\circ = T\left(\frac{\Delta G_T^\circ - \Delta H_{298}^\circ}{T}\right) + \Delta H_{298}^\circ \tag{5.129}$$

The use of the reduced Gibbs energies, which are based either on ΔH_0° or on ΔH_{298}°, is generally analogous. The function Φ for ideal gases is computed directly by means of statistical methods, which are discussed in Chapter 6, and it is dealt with more often in the original literature. But if the heat capacity in the region of low temperatures is not known, one can calculate the function Φ'

from Eq. (5.127) using the entropies known, for example, from a study of equilibria and, hence, make use of Eq. (5.129) when the corresponding relation for Φ, i.e., Eq. (5.126), is inapplicable. On the other hand, if there are values of the reduced Gibbs energy, which is based on 0°K, one can always calculate the enthalpy difference $H^\circ_{298} - H^\circ_0$ and also the function Φ' from relation (5.129).

Thus, the function Φ' may find a wide range of applications. The main argument in favour of the use of exactly this function is, however, the availability of values of ΔH°_{298} and, as a rule, the absence of heat effects referred to 0°K.* An example of the use of reduced Gibbs energies according to JANAF tables is cited on page 164 (Table 5.5).

5.6. Chemical Equilibrium

The equilibrium in systems with a variable number of particles, i.e., during the occurrence of a chemical reaction, is studied, first, on the condition that the temperature in the system is held constant and, second, if the pressure or the volume is constant. Most frequently, systems are considered at T = const and p = const when the equilibrium condition is, according to Eq. (4.21), the minimum of the Gibbs free energy, i.e.,

$$dG_{T,p} = 0 \tag{5.130}$$

or, for a finite change of the system,

$$\Delta G_{T,p} = 0 \tag{5.131}$$

We shall discuss some of the relationships that arise here for the phase transition S (rhombic; p, atm) $\rightleftharpoons$ S (monoclinic; p, atm), which may be considered a chemical reaction. As has already been mentioned in connection with Table 5.6, the temperature of the conversion of rhombic sulphur to the monoclinic modification is equal, at a pressure of 1 atm, to 368.6°K and $\Delta G_{368.6} = 0$. At a higher temperature, say at 380°K, and at the pressure indicated the monoclinic modification is more stable, $\Delta G_{380} < 0$, and the conversion from left to right is a spontaneous process. Using approximate calculations and the data of Table 5.6, we find for 380°K the pressure at which ΔG_{380} vanishes, i.e., the two modifications are again at equilibrium. With the value of the derivative $(\partial G/\partial p)_T = \underline{v}$ being known, we can write for the change of the Gibbs energies of the substance involved with increasing pressure, i.e., for the processes

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* For tables of the functions Φ, $H^\circ_T - H^\circ_0$ and S°_T, see, for example, *The Thermodynamic Properties of Individual Substances*, volumes I and II, Izd. Akad. Nauk SSSR, Moscow, 1962 (in Russian).

$$\text{S (monoclinic, 1 atm)} \overset{\Delta G_2}{=} \text{S (monoclinic, } p)$$

$$\text{S (rhombic, 1 atm)} \overset{\Delta G_3}{=} \text{S (rhombic, } p)$$

two approximate equations, respectively, $\Delta G_2 = \underline{v}_{\text{monocl}}\,(p - 1)$ and $\Delta G_3 = \underline{v}_{\text{rhomb}}\,(p - 1)$, where $\underline{v}_{\text{monocl}}$ and $\underline{v}_{\text{rhomb}}$ are the molar volumes of the monoclinic and rhombic modifications of sulphur are assumed to be constant. Thus, for the reaction under study the dependence of ΔG on pressure is expressed by the relation

$$\Delta G_1 = \Delta G_T^\circ - \Delta G_3 + \Delta G_2 = \Delta G_T^\circ + (v_{\text{monocl}} - v_{\text{rhomb}})\,(p - 1) \qquad (5.132)$$

According to Tammann, at a temperature above 100°C and increased pressures $\underline{v}_{\text{monocl}} - \underline{v}_{\text{rhomb}} = 0.4\ \text{cm}^3$. Hence, as the pressure increases the Gibbs energy of the monoclinic modification will increase more rapidly than in the case of the rhombic modification and, therefore, ΔG_1, being negative at low pressures, must change its sign with increasing p, having passed through zero. According to the data of the last line in Table 5.6 ($T = 368.6$°K) we determine $\Delta S = S_{\text{monocl}} - S_{\text{rhomb}} = 0.26$ eu and, applying the first approximation (5.104) and (5.106), we find ΔG_{380}°, i.e.,

$$\Delta G_{380}^\circ = \Delta G_{368.6}^\circ - \Delta S \Delta T = 0 - 0.26 \times 11.5 = -3 \text{ cal/mole}$$

Next we calculate the equilibrium pressure for the temperature 380°K, using relation (5.132), from the condition $\Delta G_1 = 0$ and obtain $p \approx 309$ atm.

The example given illustrates the general methods of calculating equilibria. We start with the heat effect of the reaction in question, i.e., ΔH_T°, which is usually given for 25°C. Then, in order to calculate ΔG_T° at the required temperature, use is made either of tables of reduced Gibbs energies or of the heat capacities and entropies of the participants in the reaction. And finally the change in the Gibbs energy is calculated for each participant upon its transition from the standard state to the state corresponding to the equilibrium of the reacting system. For the state of equilibrium we can write the following relation:

$$\Delta G_T = \Delta G_T^\circ + \sum_2 \Delta G_2 - \sum_1 \Delta G_1 = 0 \qquad (5.133)$$

The first term of the sum, i.e., ΔG_T°, is, for the given reaction, the quantity to be determined for each temperature. The two sums $\sum \Delta G$ for the products (2) and reactants (1) are composed, in turn, of the terms dependent on the pressure and, as will be seen later, on the composition and also on other variables that have an effect on the Gibbs energy and, hence, on the equilibrium conditions.

Let us consider an example of the calculation of equilibrium on vaporization:

$$\text{Cu (liq)} = \text{Cu (g)} \tag{5.134}$$

at 1457°K. From tables of reduced Gibbs energies we find, for the temperatures 1400 and 1500°K, the values of $(\Delta G_T^\circ - \Delta H_{298}^\circ)/T$, which are equal to -30.71 and -30.41 cal/deg·mole, respectively. By interpolation for 1457°K we find -30.57. We combine this figure with $\Delta H_{298}^\circ = 81{,}100$ cal/mole and determine $\Delta G_{1457}^\circ/1457 = 25.09$ cal/deg·mole or $\Delta G_{1457}^\circ = 36{,}560$ cal/mole. This is the standard Gibbs energy change: it corresponds to the transition of liquid copper at 1 atm to gaseous copper, which has also a pressure of 1 atm in the ideal gas state. The high positive value of ΔG shows that gaseous copper at 1 atm and 1457°K is extremely unstable as compared to liquid copper.

Let us now find the Gibbs energy change on vaporization under conditions that differ from the standard conditions. Let us consider, as an example, the process

$$\text{Cu (liq, } p, \text{ atm)} = \text{Cu (ideal gas, } p, \text{ atm)}, \ \Delta G_1 \tag{5.135}$$

We write for the standard conditions:

$$\text{Cu (liq, 1 atm)} = \text{Cu (ideal gas, 1 atm)}, \ \Delta G_T^\circ \tag{5.136}$$

In order to calculate ΔG_1 from ΔG_T° it is necessary to know the change in the Gibbs energy with pressure. Thus, for the process Cu (liq, 1 atm) = Cu (liq, p, atm) we take the function used earlier, $\Delta G' = \underline{v}(p - 1)$, where $\underline{v}$ is the molar volume of liquid copper. To determine the increment in the Gibbs energy with change in the ideal gas pressure for the process Cu (ideal gas; 1 atm) = Cu (ideal gas; p, atm), we can apply the expression for the isothermal expansion and compression of an ideal gas:

$$\Delta G'' = \underline{G}_2 - \underline{G}_1 = RT \ln \frac{p_2}{p_1} \tag{5.137}$$

Thus, for reaction (5.134), according to Eq. (5.133), we find (since $p_1 = 1$)

$$\Delta G_1 = \Delta G_T^\circ - \underline{v}(p-1) + RT \ln p \tag{5.138}$$

Since the molar volume of liquid copper is only 7.7 cm³, it is clear that the term $\underline{v}(p - 1)$ is very small for pressure less than 1 atm. The last term in Eq. (5.138) indicates that the Gibbs energy of the vapour decreases with decreasing pressure and the sign of ΔG_1 may be expected to become negative at a sufficiently low p. There is also the only pressure at which the Gibbs energies of vapour and liquid are equal. This is the saturated vapour pressure p_{sat} determined from the condition

$$0 = \Delta G_1 = \Delta G_T^\circ - \underline{v}(p-1) + RT \ln p_{\text{sat}}$$

Using the data given above, we find that

$$p_{\text{sat}} \simeq 10^{-5.48} \text{ atm} = 3.3 \times 10^{-6} \text{ atm}$$

In conclusion, we may add that we can write the following general condition of chemical equilibrium in place of Eq. (5.130) in terms of the chemical affinity [(5.74) and (5.75)]:

$$A = 0 \tag{5.139}$$

5.7. The Law of Mass Action *

Let us consider a hypothetical general reaction involving ideal gases:

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightleftharpoons \nu_1' B_1' + \nu_2' B_2' + \ldots \qquad (5.140)$$

We designate, as before, the standard Gibbs free-energy change by ΔG_T°; it corresponds to the conversion of ν_1, ν_2, etc., moles of reactants, each of which is at a pressure of 1 atm, to ν_1', ν_2', etc., moles of products, which are also at 1 atm pressure. Sometimes, in such cases it is said that one equivalent of reaction has been accomplished. Suppose that the reactants are placed in separate vessels and there are some device which take the reactants, carry out the reaction and transfer the separated products to the corresponding vessels.

Let now the reaction proceed not under standard conditions but with the reactants being at different pressures p_i. The reaction will then be accompanied by a Gibbs free-energy change other than ΔG_T°, say ΔG_T. Let us find it, taking into account the Gibbs energy change ΔG_i° of each participant in the reaction upon transition from 1 atm to the pressure p_i or vice versa. According to the already known relation, (5.133),

$$\Delta G_i = \Delta G_T^\circ + \sum_2 \Delta G_2 - \sum_1 \Delta G_1$$

Since all the substances involved are ideal gases, it follows that for a constant temperature the Gibbs energy change upon transition from the pressure p_1 to the pressure p_i will be given by

$$\underline{\Delta G}_i = RT \ln \frac{p_i}{p_1}$$

or, assuming state I to be standard, we set $p_1 = 1$ atm. Then

$$\underline{G}_i - \underline{G}_i^\circ = \Delta G_i = RT \ln p_i \qquad (5.141)$$

Employing this expression, we find, in accordance with Eq. (5.133), the Gibbs energy change of the reaction occurring under non-standard conditions:

$$\Delta G_T = \Delta G_T^\circ + \nu_1' RT \ln p_1' + \nu_2' RT \ln p_2 + \ldots$$
$$\ldots - \nu_1 RT \ln p_1 - \nu_2 RT \ln p_2 - \ldots$$

or

$$\Delta G_T = \Delta G_T^\circ + RT \ln \frac{p_1'^{\nu_1'} p_2'^{\nu_2'} \ldots}{p_1^{\nu_1} p_2^{\nu_2} \ldots} \qquad (5.142)$$

---

* The law of mass action is defined in some textbooks in terms of "active masses". This is for historical reasons as Guldberg and Waage used the term in their original publication, implying concentrations, (c, mole/litre). This law is, in fact, the "law of (equilibrium) concentrations".

There is an important case where the pressures p_i are found to be such that the reaction is not accompanied by a change in the Gibbs free energy, i.e., $\Delta G_T = 0$. In this case, one speaks of a chemical equilibrium and the corresponding pressures $(p_i)_{\text{eq}}$ are called the *equilibrium* pressures. Under these conditions

$$\Delta G_T = 0 = \Delta G_T^\circ + RT \ln \left[\frac{p_1'^{\nu_1'} p_2'^{\nu_2'} \dots}{p_1^{\nu_1} p_2^{\nu_2} \dots} \right]_{\text{eq}} \tag{5.143}$$

or

$$\Delta G_T^\circ = -RT \ln \left[\frac{p_1'^{\nu_1'} p_2'^{\nu_2'}}{p_1^{\nu_1} p_2^{\nu_2}} \right]_{\text{eq}} = \text{const} \tag{5.144}$$

The standard Gibbs energy at a given temperature is a constant quantity characteristic of the reaction. The logarithm in expressions (5.143) and (5.144) and the logarithmic expression, which we denote as K_p, i.e.,

$$K_p = \left[\frac{p_1'^{\nu_1'} p_2'^{\nu_2'} \dots}{p_1^{\nu_1} p_2^{\nu_2} \dots} \right]_{\text{eq}} \tag{5.145}$$

and which is called the *equilibrium constant* of the reaction, must therefore be also constant. As follows from Eq. (5.145), the equilibrium constant is independent of pressure since the change in the pressure of one of the substances causes such changes in the pressures of all the other substances that K_p will retain its numerical value. The same will also happen with a change in the total pressure. The equilibrium constant is a *dimensionless* quantity, though its numerical value does depend on the choice of the pressure unit (see page 176).

Expression (5.145) is one of the forms of the *law of mass action*, which was derived in a different way in 1867 by Guldberg and Waage.

Combining Eqs. (5.144) and (5.145), we can write the relation

$$\Delta G_T^\circ = -RT \ln K_p \tag{5.146}$$

which forms the basis for the thermodynamic calculation of equilibrium constants and, hence, of the equilibrium yields of products. From this relation and the data of the preceding section it is possible to find the temperature dependence of the equilibrium constant. Deferring the discussion of these important questions for a while, let us return to Eq. (5.142), substituting into it the value of ΔG_T° from expressions (5.144) and (5.146):

$$\Delta G_T = RT \ln \frac{p_1'^{\nu_1'} p_2'^{\nu_2'} \dots}{p_1^{\nu_1} p_2^{\nu_2} \dots} - RT \ln \left[\frac{p_1'^{\nu_1'} p_2'^{\nu_2'} \dots}{p_1^{\nu_1} p_2^{\nu_2} \dots} \right]_{\text{eq}} \tag{5.147}$$

or

$$\Delta G_T = RT \ln \frac{p_1'^{\nu_1'} p_2'^{\nu_2'} \dots}{p_1^{\nu_1} p_2^{\nu_2} \dots} - RT \ln K_p \tag{5.148}$$

Equation (5.147) was first derived by van't Hoff and is known as the *van't Hoff isotherm*. On its right-hand side it consists of two symmetric terms, the first of which contains arbitrary pressures, which exhibit constancy in the course of the reaction, and the second contains the equilibrium pressure of the participants in the reaction. Equations (5.147) and (5.148) transform to Eq. (5.146) if all the arbitrary pressures equal unity.

The equation for the reaction isotherm can also be written in the form

$$\Delta G_T = -RT \ln \frac{\left(\frac{p'_{1,\,\mathrm{eq}}}{p'_1}\right)^{\nu'_1} \left(\frac{p'_{2,\,\mathrm{eq}}}{p'_2}\right)^{\nu'_2}}{\left(\frac{p_{1,\,\mathrm{eq}}}{p_1}\right)^{\nu_1} \left(\frac{p_{2,\,\mathrm{eq}}}{p_2}\right)^{\nu_2}} \tag{5.149}$$

where $p_{i,\,\mathrm{eq}}$ designate equilibrium pressures and p_i are arbitrary pressures. According to what has been said, ΔG_T assumes a standard value when p_i equal unity:

$$\Delta G_T^\circ = -RT \ln \frac{\left(\frac{p'_{1,\,\mathrm{eq}}}{1}\right)^{\nu'_1} \left(\frac{p'_{2,\,\mathrm{eq}}}{1}\right)^{\nu'_2}}{\left(\frac{p_{1,\,\mathrm{eq}}}{1}\right)^{\nu_1} \left(\frac{p_{2,\,\mathrm{eq}}}{1}\right)^{\nu_2}} = -RT \ln K_p \tag{5.150}$$

that is, the equilibrium constant K_p includes not the absolute values of equilibrium pressures of the reacting substances but the dimensionless relative pressure, i.e., pressures referred to unit values of standard pressure. This is what leads to the above statement that the equilibrium constant is dimensionless. On the other hand, the numerical value of the constant will depend on the choice of pressure units, i.e., on the choice of the standard state. We assumed that the standard pressure equals 1 atm and therefore the equilibrium constant will also be expressed by means of these pressure units. But when using, for example, the standard state $p = 1$ mm Hg, each of the dimensionless fractions under the logarithm in expression (5.150), i.e., $(p_i/1)$, will change by 760 times and, hence, the numerical value of the equilibrium constant will also change.

There is a different form of the isotherm obtained from the equilibrium condition $\Delta F = 0$ for constant temperature and volume and also from the derivative $(\partial F/\partial v)_T = -p$, from which the following expression for an ideal gas is obtained:

$$F = F^\circ + RT \ln c \tag{5.151}$$

where c is the concentration (for example, moles/litre), and the standard state corresponds to $c = 1$.

Repeating the reasonings used in the derivation of Eqs. (5.145) and (5.147), we can obtain an equation for the Helmholtz free-energy change for reaction (5.140):

$$\Delta F_T = \Delta F_T^\circ + RT \ln \frac{c_1'^{\nu_1'} c_2'^{\nu_2'} \dots}{c_1^{\nu_1} c_2^{\nu_2} \dots} = RT \ln \frac{c_1'^{\nu_1'} c_2'^{\nu_2'} \dots}{c_1^{\nu_1} c_2^{\nu_2} \dots} -$$

$$- RT \ln \left[\frac{c_1'^{\nu_1'} c_2'^{\nu_2'}}{c_1^{\nu_1} c_2^{\nu_2}} \right]_{\text{eq}} \tag{5.152}$$

In the last term the ratio of the equilibrium concentrations

$$\left[\frac{c_1'^{\nu_1'} c_2'^{\nu_2'} \dots}{c_1^{\nu_1} c_2^{\nu_2} \dots} \right]_{\text{eq}} = K_c \tag{5.153}$$

is the equilibrium constant K_c expressed in terms of concentrations. Like K_p, the constant K_c is dimensionless, does not depend on concentrations, is a characteristic of a given reaction, but depends on temperature.

There also exists the following relation:

$$\Delta F_T^\circ = -RT \ln K_c$$

5.8. Open Systems. Chemical Potential. The Gibbs Fundamental Equation

The laws of thermodynamics have been applied so far to closed systems, the boundaries of which (walls) are impermeable to substances, and therefore no mass exchange with the surroundings is possible for such systems. We shall now extend the method of the thermodynamic treatment to *open systems*, which can exchange not only energy but matter as well with their surroundings.

Let us consider a multicomponent system containing variable numbers of moles $n_1, n_2, \dots, n_c$. We assume that a change in the amounts of substances may occur due either to a chemical reaction or to mass exchange across the boundary of the system. To put it differently, we shall assume that our system is open. Let us prove that with the variables S, v, $n_1, n_2, \dots, n_c$ the following relation is valid for an open multicomponent system:

$$dU = T\,dS - p\,dv + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial n_i} \right)_{S,\,v,\,n_j} dn_i \tag{5.154}$$

which is called the *fundamental Gibbs equation*. To prove it, we set $U = U(S, v, n_1, n_2, \dots, n_c)$ and, hence,

$$dU = \left(\frac{\partial U}{\partial S} \right)_{v,\,n_i} dS + \left(\frac{\partial U}{\partial v} \right)_{S,\,n_i} dv +$$

$$+ \sum_{i=1}^{c} \left(\frac{\partial U}{\partial n_i} \right)_{S,\,v,\,n_j \neq n_i} dn_i \tag{5.155}$$

but the derivatives with respect to the entropy and volume are taken here at constant numbers of moles n_i, i.e., for a system of fixed composition. Therefore, the values of these derivatives must coincide with the corresponding known derivatives for a closed system, i.e.,

$$\left(\frac{\partial U}{\partial S}\right)_{v,\,n_i}=\left(\frac{\partial U}{\partial S}\right)_v=T$$

$$\left(\frac{\partial U}{\partial v}\right)_{S,\,n_i}=\left(\frac{\partial U}{\partial v}\right)_S=-p$$

and, thus, relation (5.154) is proved. In an analogous manner, considering the functions

$$H=H\,(S,\ p,\ n_1,\ n_2,\ \ldots,\ n_c),\ F=F\,(T,\ v,\ n_1,\ n_2,\ \ldots,\ n_c)$$
$$\text{and } G=G\,(T,\ p,\ n_1,\ n_2,\ \ldots,\ n_c)$$

we can obtain the following variants of the fundamental Gibbs equation:

$$dH=T\,dS+v\,dp+\sum_i\left(\frac{\partial H}{\partial n_i}\right)_{S,\,p,\,n_j}dn_i \tag{5.156}$$

$$dF=-S\,dT-p\,dv+\sum_i\left(\frac{\partial F}{\partial n_i}\right)_{T,\,v,\,n_j}dn_i \tag{5.157}$$

$$dG=-S\,dT+v\,dp+\sum_i\left(\frac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_j}dn_i \tag{5.158}$$

We shall now prove the second important proposition, namely, the existence of the following equality:

$$\left(\frac{\partial U}{\partial n_i}\right)_{S,\,v,\,n_j}=\left(\frac{\partial H}{\partial n_i}\right)_{S,\,p,\,n_j}=\left(\frac{\partial F}{\partial n_i}\right)_{T,\,v,\,n_j}=\left(\frac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_j} \tag{5.159}$$

Proceeding from the definition of the enthalpy $H=U+pv$, we write the total differential: $dH=dU+p\,dv+v\,dp$ and substitute dU from Eq. (5.154):

$$dH=T\,dS+v\,dp+\sum_i\left(\frac{\partial U}{\partial n_i}\right)_{S,\,v,\,n_j}dn_i \tag{5.160}$$

In an analogous way, by differentiating the definitions $F=U-TS$ and $G=U-TS+pv$ and again substituting dU from Eq. (5.154), we obtain:

$$dF=-S\,dT-p\,dv+\sum_i\left(\frac{\partial U}{\partial n_i}\right)_{S,\,v,\,n_j}dn_i \tag{5.161}$$

$$dG=-S\,dT+v\,dp+\sum_i\left(\frac{\partial U}{\partial n_i}\right)_{S,\,v,\,n_j}dn_i \tag{5.162}$$

Now, comparing Eqs. (5.160), (5.161) and (5.162) with Eqs. (5.156), (5.157) and (5.158), we obtain the relations

$$\left(\frac{\partial U}{\partial n_i}\right)_{S,\,v,\,n_j}=\left(\frac{\partial H}{\partial n_i}\right)_{S,\,p,\,n_j}=\left(\frac{\partial F}{\partial n_i}\right)_{T,\,v,\,n_j}=\left(\frac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_j}\equiv\mu_i \tag{5.163}$$

which define the chemical potential of the substances of a multicomponent open or closed system. Of the series of equalities (5.163) the main one is perhaps the following:

$$\mu_i=\left(\frac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_j}=\overline{G}_i \tag{5.164}$$

It signifies that the chemical potential is at the same time the partial molar Gibbs free energy of the component. It should be noted that for a one-component single-phase system the chemical potential is equal to the molar Gibbs free energy of a pure substance, i.e.,

$$\mu=\frac{G}{n}=\underline{G} \tag{5.165}$$

The fundamental Gibbs equations can now be given the following form:

$$dU=T\,dS-p\,dv+\sum_i\mu_i\,dn_i \tag{5.166}$$

$$dH=T\,dS+v\,dp+\sum_i\mu_i\,dn_i \tag{5.167}$$

$$dF=-S\,dT-p\,dv+\sum_i\mu_i\,dn_i \tag{5.168}$$

$$dG=-S\,dT+v\,dp+\sum_i\mu_i\,dn_i \tag{5.169}$$

These equations are of great importance since they apply both to closed and open systems. They are employed for a study of chemical equilibrium in open systems and also for drawing up an entropy balance in the treatment of non-equilibrium (irreversible) processes (see Chapter 9). Let us establish the relationship between the chemical affinity A and the chemical potentials of the reactants. We now know [Eq. (5.75)] that, for example, at constant temperature and pressure $A=-(\partial G/\partial\xi)_{T,p}$ but if we put $G=G(T,\ p,\ n_1,\ n_2,\ \ldots)$, then at T and $p=\text{const}$

$$dG_{T,\,p}=\left(\frac{\partial G}{\partial n_1}\right)_{T,\,p,\,n_j}dn_1+\left(\frac{\partial G}{\partial n_2}\right)_{T,\,p,\,n_j}dn_2+\ldots$$
$$\ldots+\left(\frac{\partial G}{\partial n_c}\right)_{T,\,p,\,n_j}=\sum\mu_i\,dn_i \tag{5.170}$$

Next we can introduce into Eq. (5.170), as has been done before. the chemical variable ξ, expressing it in terms of the change in the number of moles of the components of the system which participate in any one chemical reaction:

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightleftharpoons \nu_1' B_1' + \nu_2' B_2' + \ldots \tag{5.171}$$

namely,

$$dn_i = \nu_i d\xi \tag{5.172}$$

If the change in the number of moles of the components is associated only with an insignificant progress of reaction (5.171) from left to right, then, in view of Eq. (5.172), Eq. (5.170) will assume the following form:

$$dG_{T,p} = (-\nu_1\mu_1 - \nu_2\mu_2 - \ldots + \nu_1'\mu_1' + \nu_2'\mu_2' + \ldots)\, d\xi$$

or

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \nu_1'\mu_1' + \nu_2'\mu_2' + \ldots - \nu_1\mu_1 - \nu_2\mu_2 - \ldots = \sum \nu_i\mu_i \tag{5.173}$$

Thus, the chemical affinity, which is a differential characteristic of the reaction, will be expressed as follows:

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -\sum \nu_i\mu_i \tag{5.174}$$

The summation here is carried out over all the participants in the chemical reaction. It should be noted that, although the relation $A = -\sum \nu_i\mu_i$ has been obtained for constant temperature and pressure, it is of general utility since, using other characteristic functions, it can also be obtained for systems existing under the conditions of constancy of the other variables typical of these functions, say, at constant T and v, S and v, and S and p.

The general condition of the chemical equilibrium (5.139), namely $A = 0$, will now take the following general form:

$$\sum \nu_i\mu_i = 0 \tag{5.175}$$

This condition is in the simplest form for phase equilibria, for example,

$$B_{\text{liquid}} \rightleftharpoons B_{\text{vapour}}$$

Such equilibria may be treated as a special case of the chemical equilibrium and, in accordance with Eq. (5.175), we may write the condition

$$\mu_{\text{vap}} - \mu_{\text{liq}} = 0 \text{ or } \mu_{\text{vap}} = \mu_{\text{liq}} \tag{5.176}$$

or, in general,

$$\mu_1 = \mu_2 \tag{5.177}$$

if μ_1 and μ_2 are the chemical potentials of a substance in two coexisting phases of a one-component system. Since the chemical potential of a pure substance coincides with its molar Gibbs energy, expression (5.177) is equivalent to the condition of phase equilibrium $\underline{G}_1 = \underline{G}_2$ used earlier, (5.6).

5.9. The Chemical Potential and Chemical Equilibria in Ideal Gas Mixtures. The Relationship Between Various Expressions for the Equilibrium Constant

We shall be concerned here with the application of the general condition of chemical equilibrium (5.175) to a reaction in an ideal-gas mixture at constant temperature and pressure. First, we should consider the chemical potential of a pure ideal gas. In general, for a pure substance the chemical potential is its molar Gibbs free energy, i.e.,

$$\mu = \underline{G}$$

On the basis of the derivative (5.2) used for constant temperature, the equation $p\underline{v} = RT$ and the integration from 1 atm to p we can write:

$$\mu - \mu^\circ = \underline{G} - \underline{G}^\circ = RT \ln p \tag{5.178}$$

In order to apply this relation to ideal-gas mixtures, recourse is made to Dalton's law (1802): *if two or more gases are mixed at the same temperatures and pressures, then, in the absence of a chemical reaction*: (a) the volume of the mixture is equal to the sum of the volumes of its components and (b) the temperature on mixing is not changed.

From this it follows that the pressure of a mixture of ideal gases is made up of the *partial pressures* of the components, i.e., pressures that could be produced by each of the components if it were alone in the volume of the mixture and at the same temperature:

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots = \sum p_i \tag{5.179}$$

Thus, the components of a mixture of ideal gases behave as if they were independent of one another and noninteracting.

The partial pressure of a component is determined by the total pressure of the mixture P_{total} and the molar fraction of the component:

$$p_i = P_{\text{total}} \frac{n_i}{\sum n_i} = P_{\text{total}} N_i \tag{5.180}$$

where n_i is the number of moles of a given component; N_i is its molar fraction. Also, it follows that

$$p_i V_{\text{total}} = n_i RT \tag{5.181}$$

Because of the absence of an interaction between the components of the mixture and of their independent behaviour, we can write, by analogy with Eq. (5.178), the expression for the chemical potential of one component:

$$\mu_i = \mu_i^\circ + RT \ln p_i \qquad (5.182)$$

or

$$\bar{G}_i = \underline{G}_i^\circ + RT \ln p_i \qquad (5.183)$$

where μ_i° is the chemical potential of a component in its standard state (its molar Gibbs free energy in the standard state, $\bar{G}_i^\circ$).

We can now apply the general condition of chemical equilibrium $[\sum (\mu_i \nu_i) = 0]$ to reaction (5.140) in a mixture of ideal gases which proceed at constant temperature and pressure. Substituting the expressions for the chemical potentials (5.182) into Eq. (5.175) and taking into account the constancy of the values of μ_i° at constant temperature, we deduce the law of mass action in the form (5.145) and the van't Hoff isotherm (5.148).

Analogously, utilizing the definition of the chemical potential in terms of the Helmholtz free energy

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{v,\, T,\, n_j \neq n_i} \qquad (5.184)$$

we can write for a mixture of ideal gases:

$$\mu_i = \mu_i^\circ + RT \ln c_i \qquad (5.185)$$

where c_i is the concentration of the ith component. Further, on the basis of the general equilibrium condition (5.175) we can derive the law of mass action in another form, i.e., (5.153), and also the corresponding form of the isotherm (5.152).

Let us establish the relationship between the equilibrium constants K_p and K_c. Taking advantage of the ideal-gas equation in the form $p_i = c_i RT$, which follows directly from Eq. (5.181), we substitute the values of the partial pressures into K_p:

$$K_p = \frac{c_1'^{\nu_1'} c_2'^{\nu_2'} \cdots}{c_1^{\nu_1} c_2^{\nu_2} \cdots} (RT)^{\nu_1' + \nu_2' + \cdots - \nu_1 - \nu_2} = K_c (RT)^{\Sigma \nu_i} \qquad (5.186)$$

Thus, the constants K_p and K_c will be different if $\sum \nu_i \neq 0$, i.e., if the reaction involves a change in the number of moles of gaseous substances. But if their number on the right- and left-hand sides of the stoichiometric equation is the same, for example, in the oxidation of nitrogen

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (5.187)$$

then the constants K_p and K_c are equal.

In order to calculate the equilibrium composition of a reaction mixture, it is useful to introduce the molar fractions of the participants with the aid of relation (5.180):

$$K_p = \frac{N_1'^{\nu_1'} N_2'^{\nu_2'} \ldots}{N_1^{\nu_1} N_2^{\nu_2} \ldots} P_{\text{total}}^{\Sigma \nu_i} \tag{5.188}$$

With the equilibrium constant written in this form the effect of the total pressure on the equilibrium composition of the reaction mixture is especially distinct—it is determined by the sign and magnitude of $\sum \nu_i$. When $\sum \nu_i$ is negative, as, for example, in the reaction of synthesis of ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{5.189}$$

($\sum \nu_i = -2$), then the equilibrium constant is written as

$$K_p = \frac{N_{NH_3}^2}{N_{N_2} N_{H_2}^3} P_{\text{total}}^{-2} \tag{5.190}$$

An increase in pressure leads to an increase in the molar fractions of the products—in the example given, to an increase in the yield of ammonia since on the whole K_p must retain its previous value. The equilibrium composition of the mixture in the reaction of oxidation of nitrogen will not be affected by a change in pressure within the limits of applicability of the ideal-gas laws.

The above-described effect of the pressure on the equilibrium composition is also an illustration of the manifestation of the more general le Châtelier-Braun principle. Thus, an increase in pressure in a system containing an equilibrium mixture of nitrogen, hydrogen, and ammonia will cause a process associated with a decrease in volume, i.e., in the total number of moles of the gases; in other words, it will shift the equilibrium of reaction (5.189) from left to right. It is exactly for this reason that the industrial synthesis of ammonia is carried out at high pressures reaching 1000 atm.

Sometimes the part of expression (5.188) that contains molar fractions is designated by a different special symbol:

$$K_N = \frac{N_1'^{\nu_1'} N_2'^{\nu_2'} \ldots}{N_1^{\nu_1} N_2^{\nu_2} \ldots} \tag{5.191}$$

and is called the "equilibrium constant" expressed in terms of molar fractions. It should be kept in mind that this "constant" is, as can be seen from relation (5.190), a function of pressure in a general case. This dependence will disappear when $\sum \nu_i = 0$ and

$$K_p = K_c = K_N \tag{5.192}$$

5.10. Effect of Temperature on the Equilibrium Constant

The effect of temperature on the equilibrium constant of a chemical reaction is determined by the temperature dependence of the standard Gibbs free energy of reaction, ΔG_T°, and by the relationship between this energy and the equilibrium constant. Thus, combining formulas (5.101) and (5.146), we immediately obtain the expression

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_T^\circ}{RT^2} \tag{5.193}$$

which is known as the van't Hoff isobar. The word "isobar" means that, strictly speaking, the partial derivative at constant pressure should have been written on the left since ΔH is the heat of reaction at $p = \text{const}$ and that the derivative $(\partial G/\partial T)_p = -S$ has been used in the derivation of Eq. (5.101). In other words, Eq. (5.193) describes the effect of temperature on the equilibrium constant K_p at constant pressure. This effect is determined by the sign of the heat effect. For an exothermic reaction $\Delta H < 0$, the derivative $d \ln K_p/dT$ is negative and the equilibrium constant decreases with increasing temperature. An example is the synthesis of ammonia (5.189), which is usually carried out at the lowest temperature possible.* The oxidation of nitrogen (5.187) or the conversion of methane to acetylene (5.88) are, on the contrary, endothermic ($\Delta H > 0$); for these reactions the equilibrium constant increases with an increase in temperature. The dependence $K_p = f(T)$ may also serve as an illustration of the Le Châtelier-Braun principle—an external influence on the system (an increase in temperature in this particular case) causes processes associated with the absorption of heat.

For quantitative calculations the van't Hoff isobar is integrated. Use is often made of the first approximation, assuming the heat effect to be constant. Integrating between T_1 and T_2 on this condition, we obtain the following equation:

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{\Delta H}{4.576}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5.194}$$

which is useful for calculations made over narrow temperature ranges.

We shall now deduce the integral dependence of the equilibrium constant, more exactly its logarithm, on temperature in a somewhat different manner. The temperature dependence of the standard Gibbs free energy has been derived earlier in various approximations (see Sec. 5.5). For example, in the first approximation ($\Delta H = \text{const}$) expression (5.104) is valid. Using this expression in conjunction with Eq. (5.146), we obtain:

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* For reasons which are associated with the reaction rate, "the lowest temperature possible" practically reaches 450-500°C.

$$\Delta G_T^{\circ} = -RT \ln K_p = \Delta H + JT$$

or

$$\log K_p = \frac{-\Delta H}{2.303RT} - \frac{J}{2.303R} = -\frac{\Delta H}{4.576T} - \frac{J}{4.576} \qquad (5.195)$$

Thus, according to the expression obtained the logarithm of the equilibrium constant must be a linear function of the inverse temperature:

$$\log K_p = \frac{A}{T} + B \qquad (5.196)$$

This dependence is approximate, but it often holds over a rather wide temperature range. For example, Table 5.7 presents some data for the formation of hydrogen sulphide:

$$H_2(g) + \frac{1}{2} S_2(g) \rightleftharpoons H_2S \qquad K_p = \frac{p_{H_2S}}{p_{H_2} p_{S_2}^{1/2}}$$

TABLE 5.7. **The Equilibrium Constants for the Formation of Hydrogen Sulphide at Various Temperatures**

T, °K	$1/T \times 10^4$	$\log K_p$
1023	9.775	2.052
1218	8.210	1.305
1362	7.342	0.902
1474	6.789	0.634
1667	5.999	0.257

A plot of $\log K_p$ versus $1/T$ for this reaction is given in Fig. 5.12. As can be seen, the experimental data lie satisfactorily on a straight line. The slope of the straight line

$$\tan \alpha = A = -\Delta H/4.576$$

is determined by the heat effect of the reaction. In this case

$$\tan \alpha = \frac{2.052 - 0.257}{(9.775 - 5.999) \times 10^{-4}}$$

and

$$\Delta H = -\frac{1.795 \times 4.576}{3.776 \times 10^{-4}} \approx -21{,}700 \text{ cal/mole}$$

Thus, the solution of the inverse problem is also possible: the heat effect of the reaction is determined from the slope of the straight line. Figure 5.12 also shows the approximate location of the straight line *2* for an endothermic reaction. In connection with the dependence $K_p = f(T)$ under discussion, attention should be focused on the similarity between Eqs. (5.193) and (5.196) and also Fig. 5.12 and Eqs. (5.18) and (5.21) and the corresponding straight-line dependences of the saturated vapour pressure on temperature. This similarity is not accidental since the vapour pressure may also be regarded as an equilibrium constant for the evaporation (or sublimation) process. In the latter case, however, the process is always accompanied by the absorption of heat, and therefore the straight lines for the vapour pressure have a slope of the same type as the curve *2* (see Fig. 5.12). In general, relationships of the type (5.193) or (5.194) are widely employed in physics and physical chemistry. Mention can be made, for example, of the Arrhenius equation, which describes the dependence of the reaction rate constant on temperature. Reference to this equation here is associated with the change of the temperature dependence of the approximately equilibrium concentration of activated molecules.

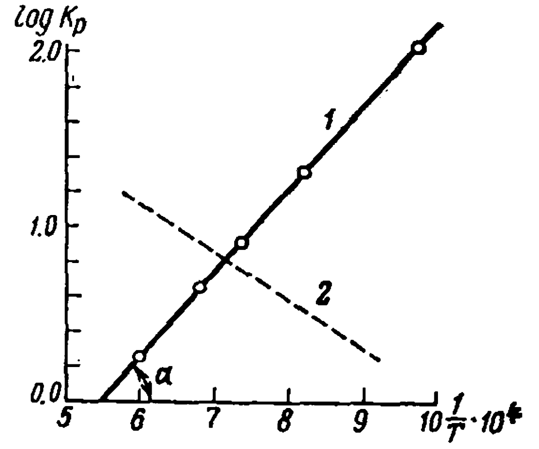

Fig. 5.12. Dependence of the equilibrium constant of the exothermic reaction of formation of hydrogen sulphide on temperature (*1*) and the corresponding dependence for the endothermic reaction (*2*).

Let us now turn to more accurate formulas for the dependence of the equilibrium constant on temperature. For instance, using the dependence $\Delta G_T^\circ = f(T)$ of the second approximation (ΔC_p = const), formula (5.107) and also relation (5.146), we write:

$$\Delta G_T^\circ = -2.303\, RT \log K_p = \Delta H_J - \Delta C_p\, 2.303\, T \log T + JT \qquad (5.196a)$$

Or, solving Eq. (5.196a) for $\log K_p$, we obtain the formula of the second approximation:

$$\log K_p = -\frac{\Delta H_J}{4.576\, T} + \frac{\Delta C_p}{1.987} \log T - \frac{J}{4.576} \qquad (5.197)$$

We shall return to this formula at a later time; at this point we shall pass immediately to the third approximation based on relation (5.113), to which there is again equated $-RT \ln K_p$. In solving

Eq. (5.197) for $\log K_p$ we write

$$\log K_p = -\frac{\Delta H_J}{4.576\,T} + \frac{\Delta a}{1.986}\log T + \frac{1}{2}\frac{\Delta b}{4.576}T + \frac{1}{6}\frac{\Delta c}{4.576}T^2 + \frac{1}{2}\frac{\Delta c'}{4.576}T^{-2} - \frac{J}{4.576} \tag{5.198}$$

Such are the analytical formulas for the calculation of the equilibrium constant at different temperatures. They derive, as can be seen, from the more general dependences $\Delta G^\circ_T = f(T)$, and it is immaterial whether $\log K_p$ is composed directly from (5.198) or ΔG°_T is calculated from (5.113) and then recalculated to give $\log K_p$ and K_p.

In equilibrium studies one can also employ other methods of determining the dependence $\Delta G^\circ_T = f(T)$ in order to arrive at the temperature dependence of the equilibrium constant. For instance, the number of arithmetic manipulations is considerably reduced when one makes use of the method of the coefficients M_i [formula (5.117)] and the table of M_i values given in Appendix 3. It is also convenient to use tables of the reduced Gibbs free energies Φ and Φ' [formulas (5.126) and (5.129)]. If, for example, tables containing values of Φ' are available for all the participants, the equilibrium constants are found on the basis of Eq. (5.129) from the relation

$$\log K_p = \frac{\Delta\Phi'}{4.576} + \frac{\Delta H^\circ_{298}}{4.576\,T} \tag{5.199}$$

The heat of reaction, ΔH°_{298}, must be found by some independent method, say, by combination of the heats of formation of the participants in the reaction in accordance with Hess's law.

5.11. Calculation of the Equilibria of Gas-Phase Reactions at Various Temperatures. Determination of Equilibrium Yields from Equilibrium Constants

We have already repeatedly made recourse to the reaction of formation of acetylene from methane (5.88). Table 5.5 contains the standard Gibbs free energies for this reaction calculated by means of the second and third approximations. Using the values obtained according to the third approximation, we tabulate the values of $\log K_p$ and K_p (see Table 5.8).

In connection with this table it is worthwhile to note the negligible value of the equilibrium constant at room temperature (25°C) corresponding to the high positive value of ΔG°_{298}. Indeed, at this temperature

$$K_p = \frac{p_{C_2H_2}\,p^3_{H_2}}{p^2_{CH_4}} = 5.38 \times 10^{-55} \tag{5.200}$$

TABLE 5.8. **The Equilibrium Constants (pressures in atm), the Equilibrium Degree of Conversion of Methane to Acetylene, x, and the Equilibrium Molar Fraction of Acetylene, $N_{C_2H_2}$, in the Reaction $2CH_4 \rightleftharpoons C_2H_2 + 3H_2$**

T, °K	$\log K_p$	K_p	$\sqrt{K_p}$	x	$N_{C_2H_2}$
298.15	−54.446	3.58×10^{-55}	5.98×10^{-28}	Small	Small
500	−27.4898	3.24×10^{-28}	1.80×10^{-14}	Small	Small
750	−13.8379	1.452×10^{-14}	1.205×10^{-7}	Small	Small
1000	−6.8446	1.366×10^{-7}	3.696×10^{-4}	0.0168	0.0083
1250	−2.6400	2.291×10^{-3}	4.787×10^{-2}	0.1884	0.0792
1500	0.17396	1.492	1.221	0.6959	0.2051
1750	2.15969	1.444×10^{2}	1.202×10	0.950	0.2435
2000	3.61729	4.143×10^{3}	6.44×10	0.990	0.2487

In order to evaluate in a more graphic manner how small this value of K_p is, let us assume that the equilibrium pressures of methane and hydrogen are equal to 1 atm. The equilibrium pressure of acetylene will then be found to equal 3.58×10^{-55} atm. If it is taken approximately that at 1 atm 6.02×10^{23} molecules are contained in 22.4 litres, then at a pressure of 3.5×10^{-55} atm one molecule of acetylene would be contained in a volume of 10^{20} cubic kilometres. In fact, this means that it is absolutely impossible to prepare acetylene from methane under these conditions. But when the temperature is raised, K_p increases rapidly and at 2000°K it reaches a high positive value, which corresponds to a high equilibrium degree* of conversion of methane to acetylene. Let us calculate these degrees of conversion from the equilibrium constants. To this end, we transform the general expression for the equilibrium constant to an equation with one unknown. In such a case, there is a choice between two principal methods: one is based on one mole of the equilibrium mixture and the other on one mole of reactant.

In the case under consideration, the second method is more convenient. Employing this method, we write the reaction in question as follows:

$$CH_4 \rightleftharpoons \frac{1}{2} C_2H_2 + \frac{3}{2} H_2 \qquad (5.201)$$

Let us assume that in a state of equilibrium x moles of methane have been undergone reaction. Hence, $(1 - x)$ moles of methane remain unreacted since we proceeded from one mole of CH_4. From x moles of methane, according to Eq. (5.201), there are formed $\frac{1}{2}x$ moles of acetylene and $\frac{3}{2}x$ moles of hydrogen. In a state of equilibrium there will be a total of $1 - x + \frac{1}{2}x + \frac{3}{2}x = 1 + x$ moles of the gases formed from one mole of methane. We write the equilibrium mole fractions of the participants in the reaction:

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* Here it would be better to use the term "pseudo-equilibrium" since equilibrium is calculated provided that only the reaction $2CH_4 \rightleftharpoons C_2H_2 + 3H_2$ takes place, i.e., on the assumption that all the other reactions, primarily the decomposition of acetylene $C_2H_2 \rightleftharpoons 2C + H_2$, are retarded.

$$N_{C_2H_2} = \frac{1}{2}\frac{x}{1+x}, \quad N_{H_2} = \frac{3}{2}\frac{x}{1+x}, \text{ and } N_{CH_4} = \frac{1-x}{1+x} \qquad (5.202)$$

Further, if the total constant pressure of the reacting mixture equals p atm, we can write the partial pressures using relation (5.180):

$$p_{C_2H_2} = \frac{1}{2}\frac{x}{1+x}P_{\text{total}}, \quad p_{H_2} = \frac{3}{2}\frac{x}{1+x}P_{\text{total}} \text{ and } p_{CH_4} = \frac{1-x}{1+x}P_{\text{total}}$$

We now substitute these values into the expression for the equilibrium constant of reaction (5.201):

$$K'_p = \sqrt{K_p} = \frac{p^{1/2}_{C_2H_2}p^{3/2}_{H_2}}{p_{CH_4}} = \frac{\sqrt{27}}{4}\frac{x^2}{1-x^2}P_{\text{total}} \qquad (5.203)$$

Thus, we have obtained a simple equation, which also specifies the effect pressure—at constant temperature a decrease in P_{total} leads to an increase in x. Introducing the notation $a = 4K'_p/\sqrt{27}$, we obtain a calculation formula, quite simple in this particular case:

$$x = \sqrt{\frac{a}{a+P_{\text{total}}}} \qquad (5.204)$$

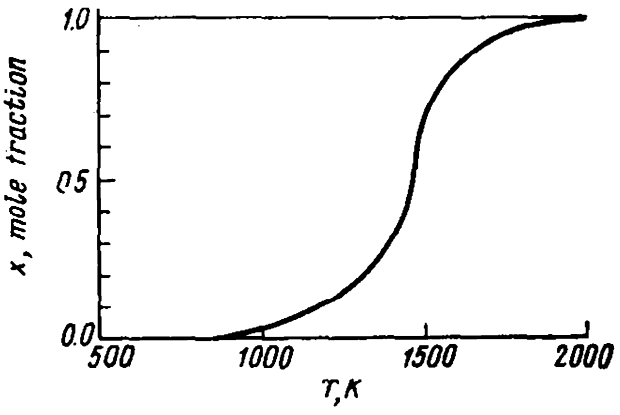

Fig. 5.13. Dependence of the equilibrium degree of conversion of methane to acetylene on temperature according to the reaction $2CH_4 \rightleftharpoons C_2H_2 + 3H_2$.

Using this formula, we calculate values of x for various temperatures, assuming $P_{\text{total}} = 1$ atm. Knowing x, we can compute, from the first of relations (5.202), the equilibrium mole fraction of acetylene, $N_{C_2H_2}$, and, consequently, the mole per cent $N_{C_2H_2} \times 100$, which coincides with the volume per cent for ideal gases. The data thus obtained are collected in Table 5.8. Figure 5.13 is a plot of x against T. We see a sigmoid curve which is characteristic of endothermic reactions of this kind and which reaches at high temperatures a limiting value of $x = 1$. Similar curves are also obtained for the conversion of other paraffinic hydrocarbons to acetylene, say, ethane and propane, but the curves corresponding to these reactions are shifted to lower temperatures due to smaller positive values of ΔH calculated per 1 mole of acetylene. Calculations of this kind form the basis for various methods of preparing acetylene from natural gas (methane) and so-called casing-head petroleum gases containing heavier hydrocarbons. In all methods based on the use of a powerful high-voltage arc, a hot flame or plasma jet, the hydrocarbon is rapidly heated for a short period of time to the temperature of the reaction. The reaction products must then be cooled rapidly, for example, by injection of atomized water, for the equilibrium of reaction (5.201) to be "frozen". The point is that at high temperatures when acetylene is more stable than methane, the carbon-hydrogen system is more stable than acetylene, i.e., the reaction

$$C_2H_2 \rightarrow 2C\ (\text{graphite}) + H_2 \qquad (5.205)$$

is spontaneous. The possibility of avoiding the decomposition of acetylene, i.e., of keeping it intact, is determined now by kinetic rather than thermodynamic factors, namely, by the relative slowness of the decomposition of the acetylene diluted with water.

Let us now turn our attention to another, even more important industrial reaction—the synthesis of ammonia from simple substances:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (5.206)$$

the thermodynamic calculation of which, carried out by Haber (1904), gave an impetus to the extensive development of the industry of fixed nitrogen. Without delving into the details, we shall give here the thermodynamic characteristics of this reaction:

$$\Delta H^\circ_{298} = -22.080 \text{ cal/2 moles } NH_3, \quad \Delta S^\circ_{298} = -47.37 \text{ eu}$$

$$\Delta C^\circ_{p,\,298} = -10.67 \text{ cal/deg}\cdot 2 \text{ moles } NH_3$$

$$\Delta G^\circ_{298} = -7957 \text{ cal/2 moles } NH_3$$

It is worthwhile to focus attention on a considerable loss in entropy in reaction (5.206) associated primarily with the double decrease in the number of moles of gas. Recall that the formation of acetylene which proceeds with a two-fold increase in the number of moles of gas is accompanied by an increase in entropy by 52.63 eu.

Let us first consider, as an example, the formulas of the second approximation based on the data given above:

$$\Delta G^\circ_T = -18{,}899 + 10.67 \times 2.303\, T \log T - 24.10\, T \qquad (5.207)$$

and

$$\log K_p = \frac{4130.0}{T} - 5.372 \log T + 5.266$$

Second, we assign values to the equilibrium constants of the reaction in question, which have been calculated by more accurate methods (Table 5.9). Finally, we calculate the composition of the equilibrium mixture at 298.15 and 800°K and at 1 and 500 atm. In such a calculation it is essential that the composition of the original mixture be specified. We take a stoichiometric mixture containing nitrogen and hydrogen in the molar ratio of 1 : 3. It is also convenient to manipulate with a stoichiometric equation containing not two but one mole of ammonia, i.e.,

$$\frac{1}{2}\,N_2+\frac{3}{2}\,H_2 \rightleftharpoons NH_3 \tag{5.208}$$

TABLE 5.9. **The Equilibrium Constants of the Synthesis of Ammonia at Various Temperatures**

$$K_p'=\frac{p_{NH_3}}{p_{N_2}^{1/2}\,p_{H_2}^{3/2}}\quad (p,\ \text{atm})$$

T, °K	K_p'	T, °K	K_p'
298.15	6.77×10^{2}	900	1.18×10^{-3}
300	6.06×10^{2}	1000	5.69×10^{-4}
400	5.63	1100	3.12×10^{-4}
500	3.01×10^{-1}	1200	1.88×10^{-4}
600	3.99×10^{-2}	1300	1.20×10^{-4}
700	9.05×10^{-3}	1400	8.47×10^{-5}
800	2.91×10^{-3}	1500	6.14×10^{-5}

We have considered above two principal methods of converting the equilibrium constant in a general form to an equation with one unknown. In this particular case, the first method is more convenient: it is based on one mole of an equilibrium gaseous mixture. Suppose that one mole of an equilibrium mixture contains y moles of ammonia. This is just the mole fraction of NH_3 since there is altogether one mole of substance. The total amount of nitrogen and hydrogen will be $1-y$ moles. There are $\frac{1}{4}(1-y)$ moles of nitrogen and $\frac{3}{4}(1-y)$ moles of hydrogen. We multiply these numbers, which, as has been said above, are equal to the mole fractions, by the total pressure; the result is the partial pressures of the components of the equilibrium mixture which we substitute into the equilibrium constant:

$$K_p'=\sqrt{K_p}=\frac{p_{NH_3}}{p_{N_2}^{1/2}p_{H_2}^{3/2}}=$$

$$=\frac{yp}{\left[\frac{1}{4}(1-y)\right]^{1/2}p^{1/2}\left[\frac{3}{4}(1-y)\right]^{3/2}p^{3/2}}=\frac{16}{\sqrt{27}}\,\frac{y}{(1-y)^2\,p}$$

Next, introducing the notation $K'_p\sqrt{27}/16 = b$, we can write a quadratic equation:

$$(bp)\,y^2 - (2bp+1)\,y + bp = 0$$

and solve it in an ordinary way:

$$y = \frac{(2bp+1) \pm [(2bp+1)^2 - 4\,(bp)^2]^{1/2}}{2bp}$$

The minus sign alone has a physical meaning since y cannot be greater than unity. The final calculation formula therefore assumes the form

$$y = \frac{2bp+1-(4bp+1)^{1/2}}{2bp} \qquad (5.209)$$

It is this formula that has been used to calculate some values of y given in Table 5.10. The data referring to the pressure 500 atm are approximate and may have only the character of estimates—at such pressures the formulas derived for ideal gases are no longer valid. These data, however, describe correctly the general tendency—the yield of ammonia increases with increasing pressure and falls off as the temperature is raised.

TABLE 5.10. **The Equilibrium Mole Per Cent (100 y) of Ammonia Under Various Conditions Calculated According to the Law of Mass Action for Ideal Gases**

T, °K	100 y by formula (5.209)		
	$p = 1$ atm	$p = 500$ atm	$p = 1000$ atm
300	93.1	99.7	99.8
500	8.22	86.7	90.3
800	0.09	25.9	37.2
1000	0.02	7.85	13.7

In modern chemistry, the reactions of dissociation of molecules into atoms are of great importance. Let us consider one reaction, namely the dissociation of the hydrogen molecule into two hydrogen atoms:

$$H_2 \rightleftharpoons H + H \qquad (5.210)$$

Evidently, the formation of free hydrogen atoms was first established by Langmuir (1911)* from an increase in the thermal conductivity of hydrogen, which surrounds a heated tungsten filament. Later, Wood (1920) proposed a method for producing hydrogen atoms based on the use of the glowing discharge at pressures of about 0.5 mm Hg. We confine ourselves to indicating the main thermodynamic characteristics of reaction (5.210), i.e., $\Delta H^\circ_{298} = 104.18$ kcal/mole, $\Delta S^\circ_{298} = 23.58$ eu (entropy units) and $\Delta G^\circ_{298} = 97.15$ kcal/mole. Table 5.11 presents the values of equilibrium constants and the degrees of dissociation α of the hydrogen molecule at various temperatures. Figure 5.14 is a plot of α against T. As can be seen from these data, a noticeable dissociation occurs only at temperatures of about 2500°K.

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* Langmuir, I., *Trans. Amer. Elektroch. Soc.*, 20, 225 (1911).

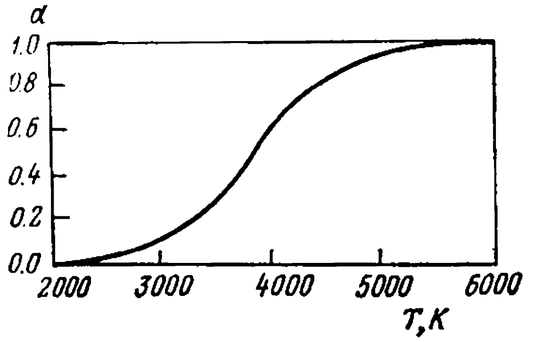

Fig. 5.14. Temperature dependence of the degree of dissociation of hydrogen molecules into atoms.

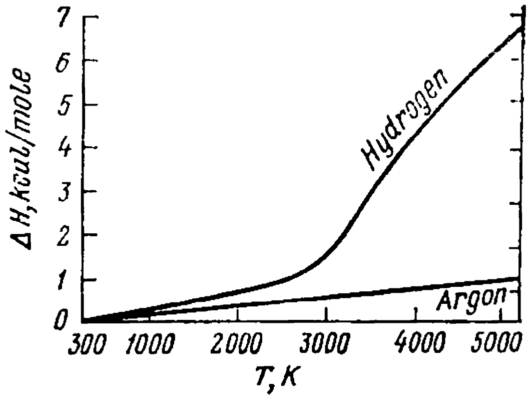

Fig. 5.15. Temperature dependence of the enthalpy ΔH of hydrogen and argon.

In this connection, it is of interest to consider Fig. 5.15, which shows an increment in the enthalpy of one mole of hydrogen upon heating from room temperature up to 5000°K. The curve displays a sharp rise at a temperature slightly above 2500°K. It is because the absorption of heat is started for the endothermic dissociation of the hydrogen molecule. For comparison, the same graph gives ΔH for argon—here over the temperature range indicated the curve is smooth. The sharp rise of the $\Delta H = f(T)$ curves is observed when the gases are heated to higher temperatures and, though the curve does not rise vertically, such inflections are treated as something like a phase transition and one speaks of the formation of the fourth state of aggregation—the plasma state. As a matter of fact, plasma is an ionized gas, though neutral as a whole since it contains equal amounts of positive and negative charges. In this sense, plasma is sometimes compared with solutions of electrolytes. However, having a high electrical conductivity, plasma conducts electricity predominantly due to electrons moving between relatively immobile ions; in this sense, plasma reminds of a metal. But the electron gas in plasma is devoid of special properties that are typical of it in a metal and are associated with the so-called quantum degeneracy.*

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* This type of degeneracy is also mentioned in Chapter 6, Sec. 6.13.

Plasma is produced by heating a gas. Use is most often made of an electric arc, electrical pulse discharge and a shock wave. Possessing a large energy reserve, plasma may serve as a medium for carrying out various endothermic reactions. The reactions of formation of acetylene [of the type (5.88)] and nitrogen oxides (5.187) carried out by such methods have been studied most extensively.

TABLE 5.11. **The Equilibrium Constants of the Dissociation of Hydrogen into Atoms, $K_p = p_H^2/p_{H_2}$ (p, atm) and Degrees of Dissociation at Various Temperatures at $p = 1$ atm**

T, °K	K_p	α
298.15	5.92×10^{-72}	1.22×10^{-36}
500	4.80×10^{-41}	3.46×10^{-21}
1000	5.10×10^{-18}	1.13×10^{-9}
1500	3.07×10^{-10}	8.76×10^{-6}
2000	2.62×10^{-6}	8.10×10^{-4}
2500	6.26×10^{-4}	1.25×10^{-2}
2600	1.46×10^{-3}	1.91×10^{-2}
2800	6.63×10^{-3}	4.07×10^{-2}
3000	2.47×10^{-2}	7.83×10^{-2}
3500	2.45×10^{-1}	0.240
4000	2.52	0.621
4500	1.18×10	0.864
5000	4.09×10	0.954
6000	2.64×10^{2}	0.992
8000	2.70×10^{3}	0.999

We shall consider in more detail the application of a jet of the low-temperature* hydrogen plasma at 5000°K for carrying out reaction (5.88). At this temperature, as can be seen from Fig. 5.15 and Table 5.11, the enthalpy of hydrogen is about 8 times higher than the enthalpy of argon, and the degree of dissociation of the hydrogen molecule into its constituent atoms reaches nearly 96 per cent. When hydrogen is cooled from 5000 to 1700°K, i.e., to the temperature at which reaction (5.88) still gives a considerable yield, one mole of hydrogen produces about 135 kcal. This quantity of heat is enough to heat the cold methane added to the plasma jet and to produce one mole of acetylene. Under the same conditions, up to 1.3-1.4 mole of C_2H_2 is formed from heavier hydrocarbons. It is essential that in the hydrogen plasma jet there can be attained much higher degrees of conversion of methane (and other hydrocarbons) into acetylene (80-85 per cent) as compared with the direct action of an electric arc on the hydrocarbon.* Therefore, the hydrogen plasma does not diminish the concentration of the acetylene produced.

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* The high-temperature plasma has a temperature of up to millions and tens of millions of degrees.

At the beginning of the 20th century the oxidation of elemental nitrogen was of considerable industrial importance:

$$N_2 + O_2 \rightleftharpoons 2NO$$

This reaction was carried out at a high temperature in electrical arcs. Later, the direct synthesis of nitrogen oxide was replaced by the oxidation of ammonia. Interest to this reaction has recently been revived due to the development of plasma chemistry. Besides, textbooks of inorganic chemistry sometimes give inaccurate data on the dependence of the concentration of nitrogen oxide on temperature. The point is that the content of nitrogen oxide in a mixture reaches values that satisfy the methods of further economic conversion of NO to nitric acid only at very high temperatures at which the molecules, primarily oxygen molecules, begin to dissociate into atoms. Therefore, one should calculate not reaction (5.187) but a set of reactions:

$$N_2 + O_2 \rightleftharpoons 2NO K_{p_1}; \quad O_2 \rightleftharpoons 2O K_{p_2}; \quad N_2 \rightleftharpoons 2N K_{p_3} \qquad (5.211)$$

On the whole, the calculation of equilibrium (5.211) is a somewhat more formidable task as compared with the earlier given examples and is based on the setting-up of five equations containing five unknown quantities. Denoting the mole fractions of NO, N, O, O_2 and N_2 by x, y, z, q, and r, respectively, and carrying out the calculation per 1 mole of the equilibrium mixture, we first write three equilibrium constants:

$$K_{p_1} = \frac{p_{NO}^2}{p_{N_2} p_O} = \frac{x^2}{rq} \qquad K_{p_2} = \frac{p_O^2}{p_{O_2}} = \frac{z^2}{q} P_{\text{total}};$$

$$K_{p_3} = \frac{p_N^2}{p_{N_2}} = \frac{y^2}{r} P_{\text{total}}$$

The fourth equation is given by the choice of one mole of the equilibrium mixture:

$$x + y + z + q + r = 1$$

And, finally, the fifth equation is obtained by using the ratio of the numbers of moles of nitrogen and oxygen in the original mixture ($N_2 : O_2 = a$):

$$a = \frac{r + 0.5x + 0.5y}{q + 0.5x + 0.5z}$$

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* The preparation of acetylene through the action of an electric arc on a gaseous hydrocarbon (electrocracking) involves the formation of considerable amounts of elemental carbon in the form of carbon black.

TABLE 5.12. **The Values of Equilibrium Constants for the Formation of Nitrogen Oxide, $N_2 + O_2 = 2NO$, K_{p_1}, the Dissociation of Oxygen into Atoms, $O_2 = 2O$, K_{p_2}, and the Dissociation of Nitrogen into Atoms, $N_2 = 2N$, K_{p_3}, at Various Temperatures (pressure in atm)**

T, °K	K_{p_1}	K_{p_2}	K_{p_3}
1000	7.26×10^{-9}	2.44×10^{-20}	8.59×10^{-44}
1500	1.03×10^{-5}	1.62×10^{-11}	3.63×10^{-27}
2000	3.88×10^{-4}	4.41×10^{-7}	7.99×10^{-19}
2500	3.41×10^{-3}	2.07×10^{-4}	8.39×10^{-14}
2800	8.63×10^{-3}	2.91×10^{-3}	1.20×10^{-11}
3000	1.44×10^{-2}	1.26×10^{-2}	1.91×10^{-10}
3500	4.02×10^{-2}	2.40×10^{-1}	4.82×10^{-8}
4000	8.64×10^{-2}	2.18×10^{0}	3.10×10^{-6}
4500	1.55×10^{-1}	1.22×10	7.96×10^{-5}
5000	2.46×10^{-1}	4.84×10	1.08×10^{-3}

The simultaneous solution of these equations yields the sought-for result—the equilibrium molar fraction x of nitrogen oxide. The calculations have been carried out, using the values of the equilibrium constants given in Table 5.12.

The results of calculations for two original mixtures ($a = 4 : 1$ and $a = 1 : 1$) and two pressures (1 atm and 50 mm Hg) are presented in Fig. 5.16. Their main feature is the presence of maxima on the curves of the percentage content of NO versus T in the temperature region of 3000-3500°K, depending on the pressure, with account taken of the dissociation. Thus, it turns out that heating the air can produce nitrogen oxide at a maximum concentration of about 5 mole per cent. At high temperatures the effect of pressure becomes important: an increase in pressure represses the dissociation of molecules into atoms and brings the concentration of nitrogen oxide to values corresponding to curves *4* and *1*.

Employing methods similar to those described above, we can also calculate the equilibria of the formation of ions in a gaseous medium, equilibria that are important in modern high-temperature chemistry; an example is

$$A \rightleftharpoons A^+ + e^- \qquad (5.212)$$

where A is a molecule; A^+ is a positively charged ion; and e^- is an electron. In calculations of equilibria of this kind the free electrons produced may be likened to particles of an ideal gas with a molar mass of $M_e = 0.0005489$. Using the formulas given in Chapter 6, we can calculate the reduced Gibbs free energy and entropy of the electron gas. The result is as follows:

$$\Phi_{el} = 11.43960 \log T - 28.2870 \text{ cal/deg·mole} \qquad (5.213)$$

and

$$S_T^\circ = 11.43960 \log T - 23.3188 \text{ cal/deg·mole} \qquad (5.214)$$

Thus, for example, the standard entropy of the electron gas is equal to 4.9878 eu at 298.15°K, i.e., it is much less than the entropies of ordinary gases. The thermodynamic characteristics of ion gases are determined in the same way*. Combining these data according to relations (5.126) and (5.146), it is possible to find the equilibrium constants if the ionization energy is also known:

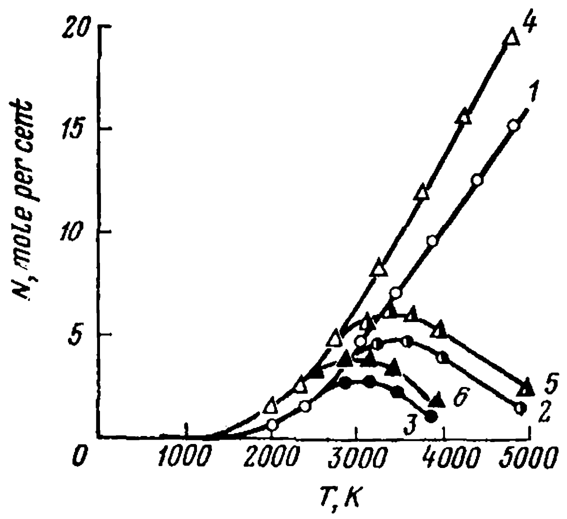

Fig. 5.16. Equilibrium concentrations of nitrogen oxide in molar per cent as a function of temperature for air ($a = 4 : 1$) and a stoichiometric mixture ($a = 1 : 1$) with and without taking into account the dissociation of both oxygen and nitrogen into atoms:

1—air wihout account taken of dissociation; 2—air with account taken of dissociation ($P_{total} = 1$ atm); 3—air with account taken of dissociation ($P_{total} = 50$ mm Hg); 4—stoichiometric mixture without account taken of dissociation ($P_{total} = 1$ atm); 5—stoichiometric mixture with dissociation taken into account ($P_{total} = 1$ atm); 6—stoichiometric mixture with account taken of dissociation ($P_{total} = 50$ mm Hg).

$$K_p = \frac{p_{A^+} p_{e^-}}{p_A} \qquad (5.215)$$

for various temperatures and to calculate, from these constants, the degree of dissociation of A into an ion and electron and also the corresponding molar fractions.

When such a relatively simple gas as nitrogen is heated to high temperatures, there are produced a number of particles, which result from the process of dissociation and ionization. Apart from N_2, there are produced N_2^+, N, N^+, N^{2+} and electrons. Figure 5.17 shows the results of calculations of this rather complex set of equilibria over the temperature range from 2000 to 28,000°K. The broken curve in this figure indicates the decrease in the density of molecular nitrogen that might occur as a result of heating alone. The very high concentration of nitrogen atoms at temperatures 7000-14,000°K should also be noted; this evidently plays an important role in the formation of nitrogen oxide in a plasma jet. Beginning with 14,000°K there appear considerable amounts of singly charged atomic ions N^+. At even higher temperatures the N^{2+} ions begin to predominate.

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* See *The Thermodynamic Properties of Individual Substances*, volumes I and II, Izd. Akad. Nauk SSSR, 1962.

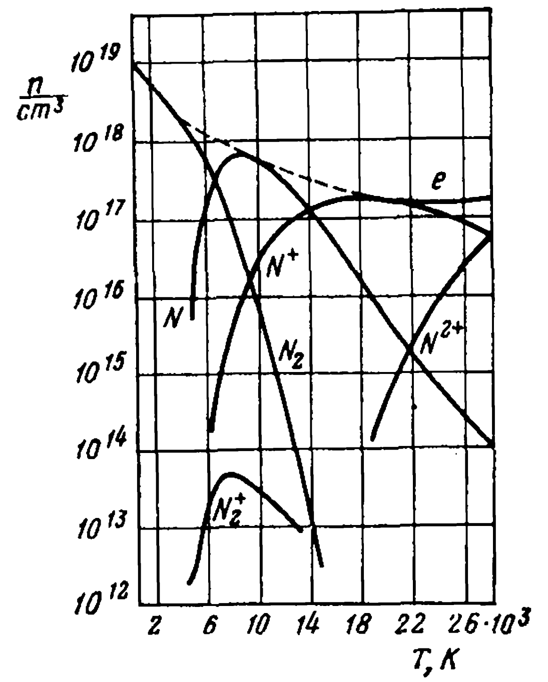

Fig. 5.17. Equilibrium concentrations of particles in nitrogen plasma at 1 atm.

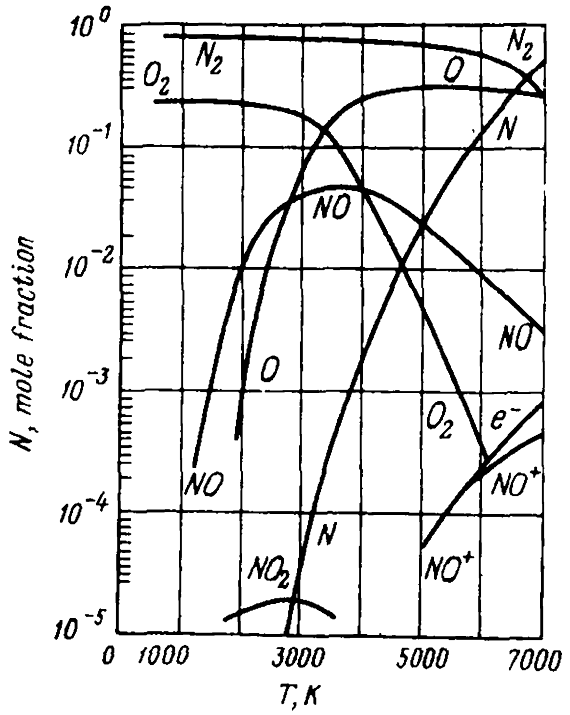

Fig. 5.18. Equilibrium concentrations of substances in air against temperature ($p = 1$ atm).

It is interesting that the concentration of molecular ions N_2^+, which appear at a temperature above 5000°K, does not increase further because of the dissociation of nitrogen molecules into atoms.

Let us now return to the formation of nitrogen oxide (5.211) and consider, in a wider temperature range, the changes in the concentration of various particles in the air plasma (see Fig. 5.18). We can clearly see a maximum on the curve for NO which amounts to 5.2 per cent at 3500°K. It is also seen that as the temperature is raised the concentration of oxygen atoms and then of nitrogen atoms increases. It is of interest that the maximum concentration of nitrogen dioxide is only 2×10^{-3} per cent at 3000°K, i.e., three orders of magnitude less than the concentration of nitrogen oxide.

5.12. Heterogeneous Chemical Equilibria

The law of mass action was deduced with the aid of the ideal gas law and is applicable, in the first place, to mixtures of ideal gases. However, without introducing substantial changes, we can also apply it to a large number of heterogeneous equilibria involving, for example, solids and gases. Let us write a generalized heterogeneous reaction:

$$\underset{\mu_1}{\nu_1 B_1 (g)} + \underset{\mu_2}{\nu_2 B_2 (sld)} + \ldots = \underset{\mu_1'}{\nu_1' B_1' (g)} + \underset{\mu_2'}{\nu_2' B_2' (sld)} + \ldots \qquad (5.216)$$

Written below the stoichiometric equation are the chemical potentials of the participants in the reaction. The general condition for chemical equilibrium in accordance with Eq. (5.175) is the following relation:

$$\sum(\mu_i \nu_i) = 0$$

As regards gases, they form a single gaseous phase and their chemical potentials may be written down in the already known form (5.182) provided that the ideal-gas law is applicable, i.e.,

$$\mu_{i(g)} = \mu_i^\circ + RT \ln p_i$$

With the solid participants the situation is the simplest when they do not form solid solutions and crystallize as separate phases, which are pure substances. For instance, in the reactions

$$\mathrm{FeO\ (sld) + H_2\ (g) \rightleftharpoons Fe\ (sld) + H_2O\ (g)} \qquad (5.217)$$

and

$$\mathrm{CaCO_3\ (sld) \rightleftharpoons CaO\ (sld) + CO_2\ (g)} \qquad (5.218)$$

the solid substances FeO and Fe and also $CaCO_3$ and CaO do not dissolve in each other, forming separate phases. In such a case the chemical potentials of individual solid substances calculated per 1 mole do not depend on their relative amounts. Therefore, at constant temperature and pressure the chemical potentials of the solid participants in the reaction are constant. Even if the pressure of the gaseous phase is changed, in most cases the change in $\mu_{i(sld)} = \bar{G}_i$ is insignificant. As we know [Eq. (5.2)], the change in Gibbs free energy with pressure is determined by the volume $[(\partial \bar{G}/\partial p)_T = \bar{v}]$, and the molar (or specific) volumes of the solids are comparatively small. On the basis of what has been said, the general condition for equilibrium may be represented in the form:

$$\sum(\mu_i \nu_i) = \nu_1' \mu_1'^\circ + \nu_1' RT \ln p_1' + \nu_2' \mu_{2(sld)}' + \ldots - \nu_1 \mu_1^\circ -$$

$$- \nu_1 RT \ln p_1 - \nu_2 \mu_{2(sld)} = 0 \qquad (5.219)$$

Rearranging Eq. (5.219), we obtain:

$$RT \ln \left[\frac{p_1'^{\nu_1'}}{p_1^{\nu_1}} \right]_{\text{eq}} =$$

$$= \nu_1 \mu_1^\circ + \nu_2 \mu_{2(\text{sld})} + \ldots - \nu_1' \mu_1'^\circ - \nu_2' \mu_{2(\text{sld})}' = \text{const} = f(T) \qquad (5.220)$$

Thus, the expression on the left-hand side of the equation is constant at constant temperature and, therefore, we may write the relation

$$\left[\frac{p_1'^{\nu_1'}}{p_1^{\nu_1}} \right]_{\text{eq}} = K_p = f(T) \qquad (5.221)$$

which expresses the law of mass action for a heterogeneous equilibrium. In other words, the equilibrium constant for reactions of this type incorporates only the partial pressures of the gaseous participants. For example, the equilibrium constant for the reaction C (graphite) + $2H_2 \rightleftharpoons CH_4$ may be written as

$$K_p = \frac{p_{\text{CH}_4}}{p_{\text{H}}^2} \qquad (5.222)$$

We shall now consider the reaction of the combustion of lime:

$$\text{CaCO}_3\ (\text{sld}) \rightleftharpoons \text{CaO}\ (\text{sld}) + \text{CO}_2\ (\text{g}) \qquad (5.223)$$

Since there is only one gaseous substance here, it follows that $K_p = p_{\text{CO}_2}$ and the equilibrium pressure of carbon dioxide is a function only of temperature. The determination of K_p gave the following values for various temperatures:

t, °C	587	703	777	819	857	898
$K_p = p_{\text{CO}_2}$, mm Hg	1	25.5	105	239	420	760

Of certain interest is the equilibrium between several crystal hydrates of salts and water vapour. For instance, in the case of cupric sulphate three equilibria can be observed:

$$\begin{aligned}
&\text{CuSO}_4\cdot5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4\cdot3\text{H}_2\text{O} + 2\text{H}_2\text{O (vap)} && K_{p_1} = p_{\text{H}_2\text{O}}^2 \\
&\text{CuSO}_4\cdot3\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4\cdot\text{H}_2\text{O} + 2\text{H}_2\text{O (vap)} && K_{p_2} = p_{\text{H}_2\text{O}}^2 \qquad (5.224) \\
&\text{CuSO}_4\cdot\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{H}_2\text{O} && K_{p_3} = p_{\text{H}_2\text{O}}
\end{aligned}$$

For example, if hydrous cupric sulphate (blue vitriol), $\text{CuSO}_4\cdot5\text{H}_2\text{O}$, is placed in the apparatus shown schematically in Fig. 5.19, and the apparatus is evacuated and heated to 50°C, the initial pressure of water vapour will be equal to 47 mm Hg (Fig. 5.20). If the vapour is then gradually pumped off from the flask, the pressure will remain unchanged for some time, but eventually it will fall in a jumpwise manner to 30 mm Hg. This is the equilibrium pressure over the trihydrate. As the vapour is pumped off further, the vapour pressure will fall to 4.4 mm Hg and then to zero. Thus, all the three equilibrium constants of the reactions are different:

$$K'_{p_1} = \sqrt{K_{p_1}} = 47 \text{ mm Hg} = p_{H_2O}$$
$$K'_{p_2} = \sqrt{K_{p_2}} = 30 \text{ mm Hg} = p_{H_2O}$$
$$K'_{p_3} = p_{H_2O} = 4.4 \text{ mm Hg} = p_{H_2O}$$

Concluding the consideration of the law of mass action, a law deduced for ideal gases, it should be noted that in essentially the same form (5.145) or (5.153) it can also be applied to equilibria in solutions. More exactly, we can apply it to infinitely dilute solutions, for which case the analogue of the ideal-gas law—the van't Hoff law of osmotic pressure—is applicable:

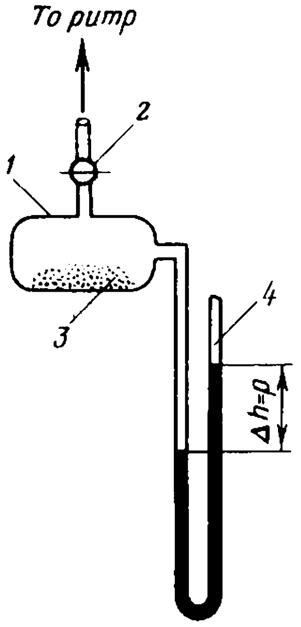

Fig. 5.19. Apparatus for study of the equilibrium vapour pressure above crystal hydrates:
1—flask; 2—stopcock; 3—crystal hydrate; 4—manometer

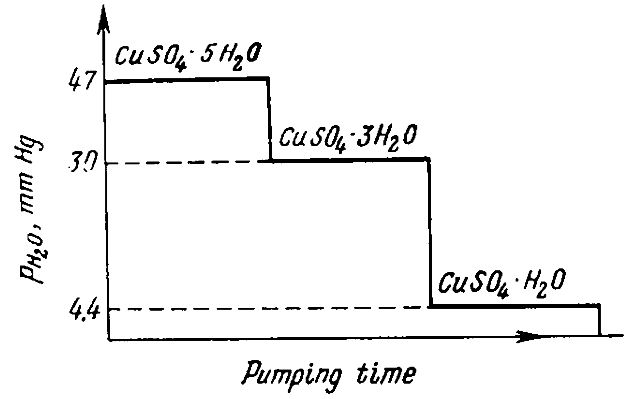

Fig. 5.20. Change in the vapour pressure above crystal hydrates of cupric sulphate at 50°C during the pumping-out of the vapour.

$$\pi_i = c_i RT \tag{5.225}$$

where π_i is the partial osmotic pressure; c_i is the concentration of a given substance; R is the universal gas constant equal to (0.08206 litre·atm/deg). The law of mass action for equilibria in solutions is used in the form:

$$K_c = \frac{c_1'^{\nu_1'} c_2'^{\nu_2'}}{c_1^{\nu_1} c_2^{\nu_2}} \tag{5.226}$$

In dealing with the dissociation of so-called weak electrolytes in solutions, say, acetic acid

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad (5.227)$$

Ostwald's dilution law is used:

$$K_c = \frac{\alpha^2}{(1-\alpha)v} \qquad (5.228)$$

where α is the degree of dissociation; $v = 1/c$ is the volume of the solution containing 1 mole of electrolyte.

5.13. Equilibrium in Real Systems. Fugacity and Activity

The law of mass action (5.145) applies, as has been said, only for ideal gases (or ideal solutions). This law may be applied to real systems only approximately; in such cases, the inaccuracy of the law must increase with increasing pressure and decreasing temperature. Below is given an example of the dependence of the equilibrium "constant" (5.206) on the pressure (at t = 450°C):

p, atm	10	30	50	100	300	600	1000
K_p	6.55×10^{-3}	6.71×10^{-3}	6.85×10^{-3}	7.20×10^{-3}	8.77×10^{-3}	1.28×10^{-2}	2.28×10^{-2}

Equilibria in real systems can in principle be studied by a method based on the use of the state equation of a real gas instead of the ideal-gas law. Namely, we can substitute v or dp, 'as determined from any equation of state, into the differential $dG = v\,dp$, and then deduce an equilibrium law which will replace the law of mass action. This method has been tested and found to be unsuccessful. Thus, first, any thermal equation of state is approximate and in order to achieve high accuracy very complex equations are required. Second, the expression of the law itself would depend on the equation of state chosen arbitrarily. Thus, there would inevitably appear various equilibrium laws, depending on the requirements and liking of the author.

A different way of solving the problem was suggested by G. Lewis, who introduced into thermodynamics the concepts of *fugacity* and *activity*.* Lewis defines the fugacity of a gas, f, with the aid of the expression derived for an ideal gas, replacing the pressure in it, i.e.,

$$\underline{G} = \underline{G}^\circ + RT \ln f \qquad (5.229)$$

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* For more detailed treatments of these concepts, see G. N. Lewis and M. Randall, *Thermodynamics*, 2nd edition, McGraw-Hill, New York, 1961.

Thus, the fugacity f is a quantity which has no definite physical significance. When substituted into the equation derived for an ideal gas, the fugacity renders it applicable to a real gas as well. Sometimes, the fugacity is called the corrected pressure, but this term, while formally reflecting the procedure, does not imply the actual meaning of the concept.

Apart from the fugacity of a pure substance defined by relation (5.229), the *partial fugacity* is also introduced instead of the partial pressure for mixtures of real gases. This is done with the aid of the expression for the chemical potential of a component in the mixture (the partial molar Gibbs free energy). Thus, instead of Eq. (5.183) or (5.182), we write:

$$\bar{G}_i = \underline{G}_i + RT \ln f_i \qquad (5.230)$$

or, in a more general form,

$$\mu_i = \mu_i^0 + RT \ln f_i \qquad (5.231)$$

The *activity* concept is introduced in an analogous way; the activity replaces the concentration of a component in a real mixture in expression (5.185), i.e.,

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (5.232)$$

In this form the equation for the chemical potential is also used for a component of a liquid solution. From the above definition of the fugacity it follows that it is measured in pressure units, most often in atmospheres. The fugacity of an ideal gas is equal to the pressure, and therefore the standard state in expressions (5.229), (5.230) or (5.231) refers to $p = f = 1$ atm. Since with increasing pressure the behaviour of a gas approaches that of an ideal gas, it follows that in the limit

$$\lim \left(\frac{f}{p}\right)_{p\to 0} = 1$$

The *activity coefficient* is widely employed; (the term *fugacity coefficient* is also used); it is given by the following relations:

$$\gamma = \frac{f}{p} \qquad (5.233)$$

or

$$\gamma = \frac{a}{c} \qquad (5.234)$$

The activity coefficient characterizes the departure of the behaviour of a gas or solution from the ideal behaviour; its numerical value may be either smaller or larger than unity. In the limit, when p or c tends to zero, the activity coefficient γ tends to unity.

Let us now describe the chemical equilibrium in real systems. From the general condition for the equilibrium of a reaction, Eq. (5.65), i.e., $\sum (\mu_i \nu_i) = 0$ [relation (5.175) and also the expression for the chemical potential, say, in the form (5.231)], we can derive an isotherm for a mixture of real gases which coincides in form with the van't Hoff isotherm, i.e.,

$$\Delta G_T = RT \ln \frac{{f'_1}^{\nu'_1} {f'_2}^{\nu'_2} \ldots}{f_1^{\nu_1} f_2^{\nu_2} \ldots} - RT \ln \left[\frac{{f'_1}^{\nu'_1} {f'_2}^{\nu'_2}}{f_1^{\nu_1} f_2^{\nu_2}} \right]_{\text{eq}} \tag{5.235}$$

where ΔG_T is the change in Gibbs free energy corresponding to one equivalent of reaction provided that the arbitrary fugacity values f_i in the first term on the right side are constant. In the second term the values of fugacity correspond to a state of equilibrium. In view of Eq. (5.235), we may write the law of mass action for a real system:

$$K_f = \left[\frac{{f'_1}^{\nu'_1} {f'_2}^{\nu'_2}}{f_1^{\nu_1} f_2^{\nu_2}} \right]_{\text{eq}} = f(T) = \text{const} \tag{5.236}$$

which coincides in form with Eq. (5.145). If one makes use of the definition of the activity coefficient (5.233), then the equilibrium constant may be represented also in the form:

$$K_f = \frac{{p'_1}^{\nu'_1} {p'_2}^{\nu'_2} \ldots}{p_1^{\nu_1} p_2^{\nu_2} \ldots} \cdot \frac{{\gamma'_1}^{\nu'_1} {\gamma'_2}^{\nu'_2} \ldots}{\gamma_1^{\nu_1} \gamma_2^{\nu_2} \ldots} = f(T) = \text{const} = K_p K_\gamma \tag{5.237}$$

We have used here the familiar symbol K_p and introduced a new one, K_γ. It is important to understand that the two quantities are not constants for real systems—they depend on the pressure and their product equal to K_f is constant at constant temperature. The procedure most frequently used in calculations of gaseous equilibria in real systems is as follows: first one determines the value of K_p at sufficiently low pressures, when $K_\gamma = 1$ and $K_p = K_f = \text{const}$. Then the activity coefficients are found for the required pressures and temperatures, this being followed by the determination of K_f under these conditions from relation (5.237). Further, assuming that Dalton's law is valid, one calculates the equilibrium extent of reaction (the equilibrium degree of conversion) and the composition of the equilibrium mixture by the method that has already been described. An example of calculation will be given later (see page 210).

In the same way, instead of the concentration equilibrium constant K_c (5.226), for a real system we can write:

$$K_a = \frac{{a'_1}^{\nu'_1} {a'_2}^{\nu'_2} \ldots}{a_1^{\nu_1} a_2^{\nu_2} \ldots} \tag{5.238}$$

Thus, the Lewis method permits us to apply to real systems (gaseous mixtures and solutions) the form of equations (primarily, the law of mass action) that has been derived for ideal systems. At the same time, this method does not introduce new principles into thermodynamics. It makes it possible not to overcome the difficulties that arise in a study of equilibria in real systems but to avoid them. The point is that in order to find the fugacities that enter into expression (5.236), one either takes advantage of some equations of state for a real gas or makes direct use of experimental p-v-T data.

We shall examine some of the relations associated with the dependence of the fugacity of a gas on pressure and temperature. The relationship between f and pressure is found by differentiating relation (5.229) with respect to the pressure and by taking account of Eq. (5.2):

$$\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{\underline{v}}{RT} \tag{5.239}$$

Or, recalling the constancy of temperature, we may write:

$$RT\, d \ln f = \underline{v}\, dp$$

and also

$$RT \ln \frac{f_2}{f_1} = \int_{p_1}^{p_2} \underline{v}\, dp \tag{5.240}$$

Using these equations, we find the numerical values of fugacity.

While dealing with the temperature dependence of the fugacity, imagine the isothermal transfer of one mole of gas from a finite pressure p and fugacity f to an extremely rarefied state with the pressure $p^* = f^*$. The latter equality means, according to the definition, that in the limit at $p \to 0$ the fugacity is equal to the pressure. The Gibbs free-energy change on this transition will be written, in accordance with Eq. (5.229), as follows:

$$\underline{G}^* - \underline{G} = RT \ln \frac{f^*}{f} \tag{5.241}$$

where $\underline{G}^*$ is the molar Gibbs free energy corresponding to the rarefied state. Differentiation of Eq. (5.141) with respect to temperature gives:

$$\frac{\partial (\underline{G}^* - \underline{G})}{\partial T} = R \ln \frac{f^*}{f} + RT \left(\frac{\partial \ln f^*}{\partial T}\right)_p - RT \left(\frac{\partial \ln f}{\partial T}\right)_p \tag{5.242}$$

The second term on the right-hand side of this equation equals zero since $f^* = p^*$, and the derivative is taken at constant pressure. Solving Eq. (5.242) for $(\partial \ln f/\partial T)_p$ and also using Eq. (5.241) and

(5.3), we get:

$$\left(\frac{\partial \ln f}{\partial T}\right)_p=\frac{1}{T}\ln\frac{f^*}{f}-\frac{1}{RT}\,\frac{\partial (G^*-G)}{\partial T}=\frac{G^*-G}{RT^2}-\frac{TS-TS^*}{RT^2}$$

or

$$\left(\frac{\partial \ln f}{\partial T}\right)_p=\frac{H^*-H}{RT^2} \qquad (5.243)$$

where H^* is the enthalpy of a mole of substance on infinite rarefaction and H is the enthalpy of a mole of substance at a finite pressure p. Note the similarity between the expression obtained and formula (5.18), which expresses the temperature dependence of the saturated vapour pressure, and recall the remarks made on page 186 in connection with the reaction isobar. According to Lewis, the quantity $H^* - H$ is the *ideal heat of vaporization.* This is the heat of vaporization or expansion of a substance into vacuum. For a real gas the difference $H^* - H$ may be associated with the Joule-Thomson effect, which is equal to zero for an ideal gas and has a finite value for various gases. As can be seen from Eq. (5.243), the quantity $H^* - H$ equals zero for an ideal gas. To estimate its value for a real gas, let us cite an example. For oxygen the heat of free expansion from 100 to 1 atm at 0°C is 340 cal/mole. Without introducing a large error, we may put $H^* - H = 340$ cal/mole, since the subsequent expansion of oxygen to $p \rightarrow 0$ is no longer associated with the absorption of heat. Thus,

$$\left(\frac{\partial \ln f}{\partial T}\right)_p=\frac{H^*-H}{RT^2}=\frac{340}{1.987\,(273.15)^2}=0.0023>0$$

To put it differently, the fugacity of oxygen at 100 atm and 0°C will increase with increasing temperature. As will be shown later, under these conditions the fugacity is lower than the pressure and on heating it will tend to assume a value equal to the pressure.

We shall discuss some of the methods of determining numerical values of the fugacity. Let us calculate the fugacity by means of the van der Waals equation, which we solve for the pressure:

$$p=\frac{RT}{(\underline{v}-b)}-\frac{a}{\underline{v}^2}$$

Next we differentiate at constant temperature:

$$dp=-\frac{RT}{(\underline{v}-b)^2}\,d\underline{v}+\frac{2a}{\underline{v}^3}\,d\underline{v}$$

and substitute the resulting value of dp into Eq. (5.240). Then, we integrate Eq. (5.240), assuming the transition of one mole of gas from the first infinitely rarefied state, characterized by the values of the variables $p^* = f^* \rightarrow 0$, $\underline{v} = \underline{v}^* \rightarrow \infty$, to the second with finite values of the variables:

$$\int_{f^*}^{f} d\ln f = -\int_{\underline{v}^*}^{\underline{v}} \frac{\underline{v}\,d\underline{v}}{(\underline{v}-b)^2} + \frac{2a}{RT}\int_{\underline{v}^*}^{\underline{v}} \frac{d\underline{v}}{\underline{v}^2} \qquad (5.244)$$

The value of the integral on the left is obvious, and the second integral on the right-hand side of the equation is equal to the difference:

$$-\frac{2a}{RT\underline{v}} + \frac{2a}{RT\underline{v}^*} \qquad (5.245)$$

To solve the first integral on the right, we denote it by J and make the substitution $\underline{v} - b = y$, whence $\underline{v} = y + b$. Consequently,

$$J = -\int_{\underline{v}^*}^{\underline{v}} \frac{y+b}{y^2}\,dy = \left| -\ln y + \frac{b}{y} \right|_{\underline{v}^*}^{\underline{v}} = \left| -\ln(\underline{v}-b) + \frac{b}{\underline{v}-b} \right|_{\underline{v}^*}^{\underline{v}} = -\ln(\underline{v}-b) + \ln(\underline{v}^*-b) + \frac{b}{\underline{v}-b} - \frac{b}{\underline{v}^*-b}$$

Thus, taking cognizance of Eq. (5.245), we can write Eq. (5.244) in the form:

$$\ln f - \ln f^* = -\ln(\underline{v}-b) + \ln(\underline{v}^*-b) + \frac{b}{\underline{v}-b} - \frac{b}{\underline{v}^*-b} - \frac{2a}{RT\underline{v}} + \frac{2a}{RT\underline{v}^*}$$

We rearrange the relation obtained, dropping the zero-tending terms with $\underline{v}^*$ in the denominator, neglecting the constant b as compared with $\underline{v}^*$, introducing RT/p^* in place of $\underline{v}^*$ and, finally, taking into account the equality $\ln f^* = \ln p^*$; we obtain

$$\ln f = \ln\frac{RT}{\underline{v}-b} + \frac{b}{\underline{v}-b} - \frac{2a}{RT\underline{v}} \qquad (5.246)$$

This is what is known as the van der Waals equation for the fugacity of a gas. Using this equation and knowing the constants a and b, it is not difficult to find the fugacity of a gas. Calculations based on the van der Waals equation is seldom used since both the equation and the results obtained are approximate.

We shall discuss here two graphical methods of determining the fugacity. We assume that there are compressibility data for a gas of interest, i.e., values of volumes for a number of pressures and temperatures and, hence, we can plot the isotherm $p = f(v)$ (curve b in Fig. 5.21). It is then easy to construct on the same graph the ideal isotherm $p = RT/v$ (curve a). We choose two pressures, p and p', and draw the corresponding isobars. Then, in accordance with Eq. (5.240) and Fig. 5.21 we have:

$$RT \ln \frac{f}{f'} = \int_{p_1}^{p_2} v\,dp = \text{area } 122'1' = \text{area } 133'1' - \text{area } 233'2'$$

or

$$RT \ln \frac{f}{f'} = RT \ln \frac{p}{p'} - A \tag{5.247}$$

Here the area of the figure (133'1') is limited by an ideal isotherm and A denotes the area outlined by the isotherms and the isobars p and p'. We move now the isobar p' downward, as a result of which p' will turn into $p^* \to 0$ and $f' = f^* \to p^*$. The area A will increase to A^*. Thus, we finally obtain:

$$RT \ln f = RT \ln p - A^* \tag{5.248}$$

Hence, to determine the fugacity of a gas at a given pressure p we are to measure the area enclosed between the two isotherms from the specified pressure p to $p = 0$ or $v = \infty$. The latter circumstance is an inconvenience of the method under discussion because it is difficult to plot isotherms in the region of large volumes and to decide where they are to be interrupted.

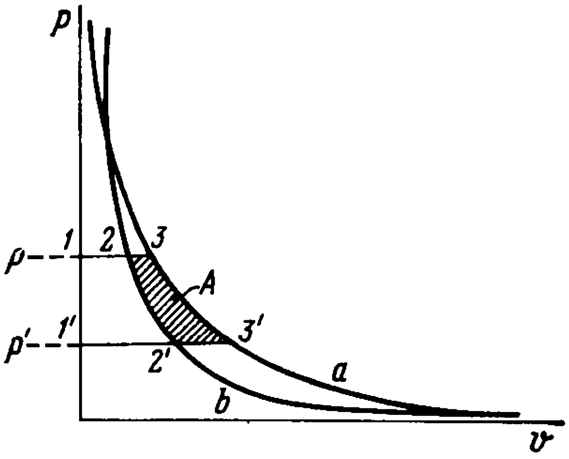

Fig. 5.21. Graphical determination of the fugacity of a gas (the first method):
a—ideal isotherm; *b*—real isotherm.

This shortcoming is absent in another graphical method, which is also based on a knowledge of the actual values of p-v-T and the difference α between the ideal volume RT/p and the actual volume v, i.e.,

$$\alpha = \frac{RT}{p} - v \quad \text{and} \quad v = \frac{RT}{p} - \alpha \tag{5.249}$$

Thus, according to Eq. (5.240), we can write:

$$RT \ln \frac{f}{f'} = \int_{p'}^{p} \left(\frac{RT}{p} - \alpha\right) dp = RT \ln \frac{p}{p'} - \int_{p'}^{p} \alpha\,dp$$

TABLE 5.13. **The Fugacities of Oxygen and Carbon Dioxide**

O_2 ($T = 273.15$°K)			CO_2 ($T = 333.15$°K)		
p, atm	f, atm	$\gamma = \frac{f}{p}$	p, atm	f, atm	$\gamma = \frac{f}{p}$
50	48.0	0.960	25	23.2	0.928
100	92.5	0.925	50	42.8	0.86
200	174.0	0.870	100	70.4	0.70
400	338.0	0.85	200	91.0	0.45
600	540	0.90	300	112	0.37

If we now turn to infinite rarefaction, assuming that p' tends to $p^* = 0$ and $f' \rightarrow f^* = p^*$, then

$$RT \ln f = RT \ln p - \int_0^p \alpha \, dp \qquad (5.250)$$

The calculation of the fugacity by this method consists in plotting the dependence $\alpha = f(p)$ and determining the area* of the figure obtained.

An approximate configuration of the resulting curve is shown in Fig. 5.22; when the value of $p = 0$ is approached, the curve has to be extrapolated, which is not difficult to do because the path of the curve in the region of low pressures is linear (and even horizontal). Table 5.13 presents fugacity values for oxygen at 0°C and for carbon dioxide at 60°C as calculated from the van der Waals equation of state. As can be seen, in all the cases given the fugacity is lower than the pressure and the coefficient γ is less than unity. But this is not always the case. Even in the case of oxygen it is seen that as the pressure increases the activity coefficient passes through a minimum. At even higher pressure the coefficient γ will reach unity and even exceed it. For example, for carbon monoxide at a pressure of 1200 atm the fugacity equals 2663, i.e., $\gamma \cong 2.22$ by far exceeds unity.

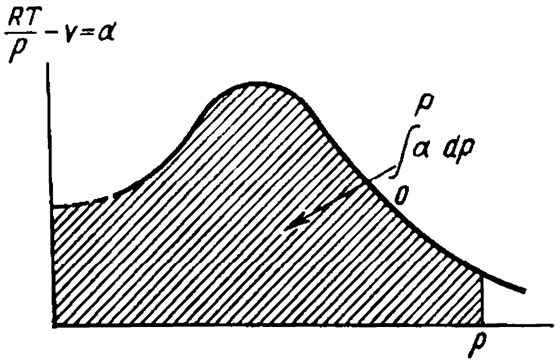

Fig. 5.22. Graphical determination of the fugacity of a gas (the second method).

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* One of the methods of determining the area consists in weighing the figure cut out of the drawing and comparing its weight with the weight of the paper of known area.

The determination of fugacity by means of more or less accurate methods is time-consuming in each particular case. The task is facilitated through the use of various types of tables containing calculated data. Such tables, however, cannot cover all data that may be required in practice. Therefore, in those cases when no high accuracy is required, recourse is made to an approximate method of evaluating f and γ based on the *principle of corresponding states* (see Chapter 1). Corresponding states are the states of substances at the same reduced temperature and pressure, i.e., the same

$$\tau = \frac{T}{T_{cr}} \quad \text{and} \quad \pi = \frac{p}{p_{cr}} \tag{5.251}$$

where T and p are the temperature and pressure; T_{cr} and p_{cr} are the critical values of these parameters for a given substance. The corresponding states of a substance must in principle be the same, but, as a matter of fact, they are found to be similar—the principle of corresponding states is approximate. For example, at $\tau = 1$ and $\pi = 1$ substances are in a critical state. At $\tau > 1$ the substance is a gas and does not convert into a liquid at any pressure. At $\tau < 1$ the substance may be either in the vapour or the liquid state, depending on the pressure.

One of the corollaries of the principle of corresponding states is the statement that in the corresponding states of substances their activity coefficients are the same. This allows us to compile tables for all substances and plot graphs of $\gamma = f(\tau, \pi)$. Figure 5.23 presents the $\gamma = f(\pi)$ isotherms (τ = const). In using these graphs one must evidently find first the corresponding isotherm and then from it on the ordinate to look for the value of γ for the required pressure found along the abscissa. The approximate nature of the method has been established for a large number of substances (several hundreds) and it has been found that hydrogen, helium and neon depart significantly from the general scheme. In calculating the reduced temperature and pressure for these substances one should introduce an empirical correction, equal to 8 atm or 8 deg, into the critical values, i.e.,

$$\tau = \frac{T}{T_{cr}+8} \quad \text{and} \quad \pi = \frac{p}{p_{cr}+8}$$

Let us now consider an example of approximate calculation of the equilibrium of the ammonia synthesis at a temperature of 800°K and the pressures 300 and 600 atm. From the standard Gibbs free energy of the reaction we find K_p and, since the standard state is the ideal-gas state, we also determine K_f, which retains its value at high pressures. With a further approximation we assume that the activity coefficients depend on the total pressure of the reacting mixture and determine them using the reduced pressures found from the

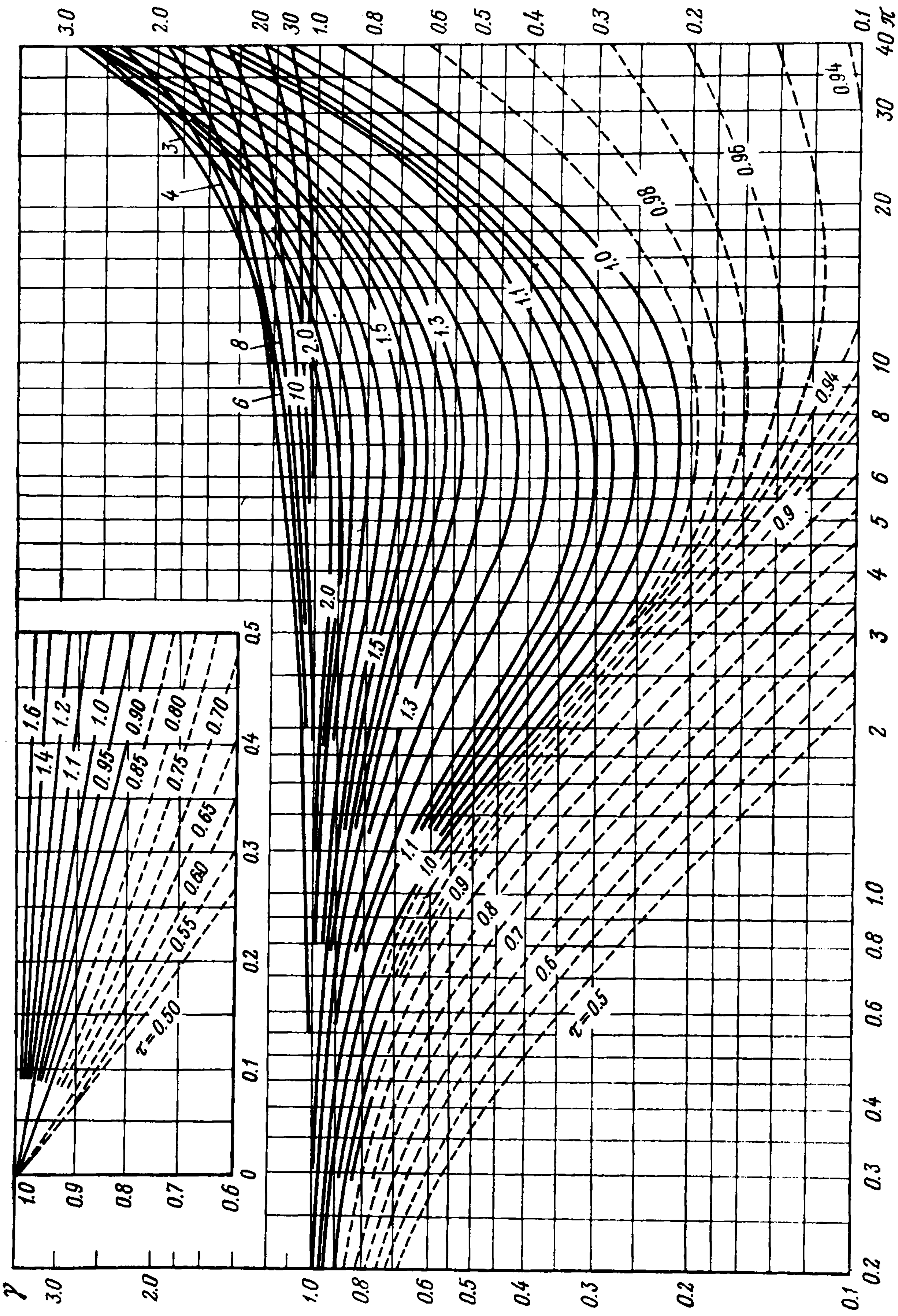

Fig. 5.23. Dependence of the activity coefficient on the reduced values of pressure and temperature.

relation

$$\pi_i = \frac{P_{\text{total}}}{p_{\text{cr}(i)}} \tag{5.252}$$

The activity coefficients obtained by the principle of corresponding states for pure gases are extended to gaseous mixtures with the aid of the Lewis-Randall postulate on the partial fugacity: $f_i = f_{i0}N_i = \gamma_{i0}N_iP_{\text{total}}$, where $f_{i0} = \gamma_{i0}P_{\text{total}}$ is the fugacity of a pure gas at the total pressure P_{total}; γ_{i0} is the activity coefficient of the ith component in a pure state. We tabulate the reduced pressures and temperatures and also the coefficients γ_i of the substances participating in the reaction (see Table 5.14): $N_2 + 3H_2 = 2NH_3$. From the activity coefficients found from the graph (see Fig. 5.23) we calculate $\log K_\gamma$ (300 atm) $= \bar{1}.8968$ and $\log K_\gamma$ (600 atm) $= \bar{1}.2640$ and, from relation (5.237), we also find the values of K_p, assuming $K_f = 2.91 \times 10^{-3}$: $K_p = 3.69 \times 10^{-3}$ for 300 atm and $K_p = 1.58 \times 10^{-2}$ for 600 atm.

TABLE 5.14. **Calculating the Ammonia Equilibrium at High Pressures ($T = 800°K$)**

Substance	$p = 300$ atm			$p = 600$ atm		
	π	τ	γ	π	τ	γ
H_2	$\frac{300}{12.8+8}=14.4$	$\frac{800}{33.5+8}=19.3$	1.08	$\frac{600}{12.8+8}=28.8$	19.3	1.18
N_2	$\frac{300}{33.5}=8.95$	$\frac{800}{126.1}=6.34$	1.152	$\frac{600}{33.5}=17.90$	6.34	1.30
NH_3	$\frac{300}{111.5}=2.69$	$\frac{800}{405.5}=1.97$	0.95	$\frac{600}{111.5}=5.38$	1.97	0.92

Using formula (5.209), we can now find the equilibrium values of y, the molar fraction of ammonia in the mixture.

5.14. Phase Equilibria at High Pressures

In this section we shall consider the effect of pressure on the equilibria

$$\text{liquid} \rightleftharpoons \text{vapour and solid} \rightleftharpoons \text{vapour} \tag{5.253}$$

Proceeding from the Lewis concepts, we extend the concept of fugacity. We know that phase transitions are characterized by the equality of molar Gibbs free energies. If the standard states for two states of a substance (say, for liquid and vapour) are assumed to be identical, then in agreement with Eq. (5.229) the equality of the Gibbs energies will lead to the equality of the fugacities, i.e., for equilibria (5.253) we may write:

$$f_{\text{liq}} = f_{\text{vap}} \quad \text{and} \quad f_{\text{sld}} = f_{\text{vap}} \tag{5.254}$$

From these relations it follows that the fugacity of a liquid or solid is equal to the fugacity of the vapour in equilibrium with them. Frequently, when the vapour pressure is low and may be equated to the fugacity, the vapour pressure will be a measure of the fugacity of the liquid (or solid), i.e.,

$$f_{\text{liq}} \approx p_{\text{vap}} \tag{5.255}$$

For example, at 25°C the pressure of saturated water vapour is $p_{H_2O} = 24.54$ mm Hg (0.03229 atm)*, i.e., is negligible. Therefore, for liquid water too at low pressures we may write

$$f_{H_2O\,(\text{liq})} = 0.03229 \quad \text{atm} = p_{H_2O\,(\text{vap})} \tag{5.256}$$

In this connection we may say that the fugacity is, as it were, *a measure of the tendency for a substance to leave a given phase and to enter another*. For an ideal gas this measure is the pressure and for a real gas and condensed states it is the fugacity.

Further, using the concept of the fugacity of a liquid, we can approach the question of the dependence of the equilibrium pressure of its vapour on the pressure exerted on the liquid. A good example is water—its fugacity at a low pressure is known, Eq. (5.256). Let us find, for example, its fugacity at 1000 atm. According to Eq. (5.240), we can write for constant temperature:

$$RT \ln \frac{f_2}{f_1} = \int_{p_1}^{p_2} v\, dp \tag{5.257}$$

where f_1 and f_2 are the fugacities at pressures p_1 and p_2, respectively. Upon integration of Eq. (5.257) we make use of the compressibility factor of a liquid (or a solid):

$$\beta \equiv -\frac{1}{v_0} \left(\frac{\partial v}{\partial p} \right)_T$$

from which we determine the dependence of the volume on the pressure by integrating approximately from 0 to p and from v_0 to v, assuming β to be a constant quantity:

$$\int_{v_0}^{v} dv = -\beta v_0 \int_{0}^{p} dp \quad \text{or} \quad v = v_0 (1 - \beta p)$$

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* *Chemist's Handbook*, vol. I, Goskhimizdat, Moscow, 1963, p. 729.

We substitute this pressure dependence of the volume into the integral of (5.257) and, as a result, we have:

$$RT \ln \frac{f_2}{f_1} = v_0 \int_{p_1}^{p_2} (1-\beta p)\, dp = v_0 \left[(p_2 - p_1) - \frac{1}{2} \beta (p_2^2 - p_1^2) \right] \quad (5.258)$$

For liquid water $v_0 = 18.07$ cm^3/mole and $\beta = 45 \times 10^{-6}$ atm^{-1}. Thus, taking cognizance of Eq. (5.256), we can write:

$$RT \ln \frac{f_{1000}}{0.03229} = 18.07 \left[(1000-0.03) - \frac{1}{2} 45 \times 10^{-6} (1000^2 - 0.03^2) \right] =$$

$$= 17{,}660 \text{ cm}^3 \cdot \text{atm/mole} = 428 \text{ cal/mole}$$

from which

$$f_{1000} = 0.03229 \exp \left(\frac{428}{1.987 \times 298.15} \right) = 0.0665 \text{ atm}$$

Thus, the fugacity of liquid water increases by about two times when the pressure is raised to 1000 atm. Since $f_{\text{liq}} = 0.0654$ atm is still small, we may identify this value with the equilibrium vapour pressure of liquid water compressed to 1000 atm. We can imagine that the liquid is compressed by a piston, which is permeable to the vapour and impermeable to the liquid. The vapour pressure above the piston will be equal to the calculated value. More real is the compression of the liquid with the aid of a foreign neutral gas (but in this case the gas must not dissolve strongly in the liquid).* The increase in the fugacity of a liquid with increasing pressure of a gas plays an important role in high-pressure technology, for example, in the synthesis of ammonia, where the gas mixture is contaminated with the vapour of an oil—the lubricant used for the compressor and circulating pump.

In a similar way we can consider the dependence of the vapour pressure of a solid on the external pressure if its compressibility is known.

5.15. Entropy and Chemical Thermodynamics

In this section emphasis is placed on the particular importance of the entropy in the thermodynamics of equilibrium states and the subordinate role of some functions (the Gibbs free energy G and the Helmholtz free energy F).

The second law of thermodynamics is generally formulated, as known, with the aid of a special property of the system called the entropy S:

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* The vapour pressure of liquid is reduced by the dissolution of the gas. Thus, we have here two opposite effects. The first is, however, stronger for ordinary gases.

$$dS \geqslant \frac{\delta Q}{T} \tag{5.259}$$

or, for isolated systems,

$$dS \geqslant 0 \tag{5.260}$$

In both these relations the equality refers to equilibrium (reversible) processes and the inequality to non-equilibrium (irreversible) processes. Thus, relation (5.260) defines the criterion of a possible spontaneous change of the system—an increase in entropy, and the equilibrium criterion for an isolated system, i.e., the entropy maximum.

On the other hand, one of the principal tasks in chemical thermodynamics is to predict the possible direction of a chemical reaction, to calculate chemical equilibria and to determine the possible yields of reaction products. This task can, in principle, be solved only on the basis of relation (5.260). In other words, we wish to show that the introduction of the concepts of the Gibbs free energy and the Helmholtz free energy into thermodynamics does not lead to anything new and is only used for the practical convenience of calculations. We shall try to solve the problem of chemical equilibrium by using only the properties of the entropy. For the sake of simplicity, we confine ourselves to the consideration of reactions in an ideal gaseous mixture at constant temperature and pressure.

The pressure dependence of the entropy of n moles of an ideal gas at constant temperature may be expressed by the formula

$$S = nS^\circ - nR \ln p \tag{5.261}$$

where S° is the standard molar entropy of a given gas (i.e., at $p = 1$ atm). As we know, Eq. (5.261) may be used to calculate the entropy of a component of an ideal gaseous mixture, but the total pressure p should be replaced in this case by the partial pressure p_i and, accordingly, S should be replaced by S_i. The total entropy of the mixture will be equal to the sum of the thus calculated entropies of the components.

Consider a system in which the following reversible chemical reaction can occur:

$$H_2 + I_2 \rightleftharpoons 2HI \tag{5.262}$$

Let this system contain n_1 moles of hydrogen, n_2 moles of iodine and n_3 moles of hydrogen iodide. The system is maintained, by means of a suitable (sufficiently capacious) heat reservoir, at constant temperature T. The heat reservoir is considered to be part of the entire large system.

Reaction (5.262), which proceeds at constant pressure in accordance with the condition assumed, does not involve a change in volume (the number of moles is not changed during the course of the reaction) and, hence, there is no exchange of work with other systems. In other words, our system, which consists of a gaseous mixture and a heat reservoir, may be treated as an isolated system ($v =$ const and $U =$ const). Therefore, any spontaneous change in such a system must, in conformity with Eq. (5.260), be accompanied by an increase in the total entropy, i.e., the sum of the entropies of the gas and reservoir must increase, though the entropy of the gaseous mixture or reservoir taken separately may diminish.

Let us find the entropy of the gaseous mixture. We assume that α moles of hydrogen have reacted. Upon completion of the reaction the mixture will contain $n_1 - \alpha$ moles of hydrogen, $n_2 - \alpha$ moles of iodine and $n_3 + 2\alpha$ moles of hydrogen iodide. We write the mole fractions:

$$N_{H_2} = \frac{n_1 - \alpha}{n_1 + n_2 + n_3}; \quad N_{I_2} = \frac{n_2 - \alpha}{n_1 + n_2 + n_3}; \quad N_{HI} = \frac{n_3 + 2\alpha}{n_1 + n_2 + n_3}$$

Multiplying the mole fractions by the total pressure of the gaseous mixture p, we obtain the partial pressures of the components with the aid of which we can write, by means of formula (5.261), for the entropies of the components and the entropy of the entire mixture as a whole:

$$S_{\text{mixture}} = S_{H_2} + S_{I_2} + S_{HI} = (n_1 - \alpha) S^{\circ}_{H_2} - (n_1 - \alpha) R \ln \frac{n_1 - \alpha}{n_1 + n_2 + n_3} p +$$
$$+ (n_2 - \alpha) S^{\circ}_{I_2} - (n_2 - \alpha) R \ln \frac{n_2 - \alpha}{n_1 + n_2 + n_3} p + (n_3 + 2\alpha) S^{\circ}_{HI} -$$
$$- (n_3 + 2\alpha) R \ln \frac{n_3 + 2\alpha}{n_1 + n_2 + n_3} p \qquad (5.263)$$

Reaction (5.262) proceeds with the absorption of heat ($\Delta H^{\circ}_{298} = 6.2$ kcal/mole). To maintain the temperature constant this heat must be supplied to the gaseous mixture by the heat reservoir. The heat effects of the gaseous mixture and reservoir will be equal in absolute magnitude but opposite in sign. If ΔH° refers to one equivalent of reaction, i.e., to the formation of two moles of hydrogen iodide, the heat effect of the gaseous mixture will be equal to $\alpha \Delta H^{\circ}$ and that of the reservoir to $-\alpha \Delta H^{\circ}$. Since the heat exchange occurs at constant temperature, the reaction may be considered to be an equilibrium process, and the change of the entropy of the reservoir can be determined from formula (5.259):

$$\frac{Q_T}{T} = -\frac{\alpha \Delta H}{T}$$

If the entropy of the heat reservoir is denoted by S°_{res} before the reaction and by S_{res} after the reaction, then

$$S_{\text{res}} = S^{\circ}_{\text{res}} - \frac{\alpha \Delta H^{\circ}}{T}$$

The total entropy of the system, S_{total}, is equal to the sum of the entropies of the gaseous mixture and the heat reservoir:

$$S_{\text{total}} = (n_1-\alpha)\,S^{\circ}_{\text{H}_2} - (n_1-\alpha)\,R\,\ln\frac{n_1-\alpha}{n_1+n_2+n_3}\,p + \\ + (n_2-\alpha)\,S^{\circ}_{\text{I}_2} - (n_2-\alpha)\,R\,\ln\frac{n_2-\alpha}{n_1+n_2+n_3}\,p + (n_3+2\alpha)\,S^{\circ}_{\text{HI}} - \\ - (n_3+2\alpha)\,R\,\ln\frac{n_3+2\alpha}{n_1+n_2+n_3}\,p + S^{\circ}_{\text{res}} - \frac{\alpha\Delta H^{\circ}}{T} \qquad (5.264)$$

We may now determine the equilibrium state, to which, in accordance with Eq. (5.260), there corresponds the entropy maximum, i.e., $dS = 0$. To find the maximum we differentiate S_{total}, i.e., expression (5.264), with respect to α at constant p and T and equate the derivative to zero*:

$$\left(\frac{\partial S_{\text{total}}}{\partial\alpha}\right)_{p,T} = -S^{\circ}_{\text{H}_2} + R\ln\frac{n_1-\alpha}{\sum n}\,p + R - S^{\circ}_{\text{I}_2} + R\ln\frac{n_2-\alpha}{\sum n}\,p + R + \\ + 2S^{\circ}_{\text{HI}} - 2R\ln\frac{n_3-2\alpha}{\sum n}\,p - 2R - \frac{\Delta H^{\circ}}{T} = 0$$

Or, after performing simple transformations, we obtain the relation

$$RT\ln\left[\frac{(n_3+2\alpha)^2}{(n_1-\alpha)\,(n_2-\alpha)}\right]_{\text{eq}} = -\Delta H^{\circ} + T\,(2S^{\circ}_{\text{HI}} - S^{\circ}_{\text{H}_2} - S^{\circ}_{\text{I}_2}) = \\ = -\Delta H^{\circ} + T\Delta S^{\circ} \qquad (5.265)$$

where α stands for the amount of the reacted substance corresponding to a state of equilibrium; ΔS° is the standard entropy of the reaction.

Thus, according to Eq. (5.265), in order to determine the equilibrium state of the reacting system it is necessary to know, apart from the original composition of the mixture, the heat of the reaction at a given temperature, $Q_r = \Delta H^{\circ}$, and the molar standard entropies of the participants in the reaction at the same temperature.

At a specified temperature the expression on the right-hand side of Eq. (5.265) is constant and so is the logarithmic expression on the left. It can be rearranged by using the relationship between the partial pressures of the components and the mole fractions that has been mentioned at the beginning of this section:

$$RT\ln\left[\frac{p^2_{\text{HI}}}{p_{\text{H}_2}p_{\text{I}_2}}\right]_{\text{eq}} = -(\Delta H^{\circ} - T\Delta S^{\circ}) \qquad (5.266)$$

In view of the constancy of the logarithmic expression, we may write:

$$\frac{p^2_{\text{HI}}}{p_{\text{H}_2}p_{\text{I}_2}} = K_p = \text{const at } T = \text{const} \qquad (5.267)$$

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* The constancy of pressure is guaranteed by the fact that the number of moles in reaction (5.262) remains unchanged.

and K_p may be called the equilibrium constant. Combining relations (5.266) and (5.267), we obtain the already known relationship between the equilibrium constant and the standard enthalpy and entropy changes:

$$-RT \ln K_p = \Delta H^\circ - T\Delta S^\circ \tag{5.268}$$

A different route is usually chosen in courses of thermodynamics. Namely, the Helmholtz free energy F and the Gibbs free energy G are introduced in passing over to chemical systems; they are determined with the aid of the equilibrium condition for non-isolated isothermal systems and the law of mass action is deduced. The latter route is simpler since it requires less unwieldy computations. This method, may, however, be dispensed with. The law of mass action is derived in the form of relation (5.267) on the basis of the entropy maximum without using any new concepts.

We can now combine two paths into one. The Gibbs free energy is defined as the function $G = H - TS$. The change in G at constant temperature is written as the difference in G in two states: $H_1 - TS_1$ and $H_2 - TS_2$:

$$\Delta G^\circ = G_2^\circ - G_1^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5.269}$$

Comparing Eqs. (5.268) and (5.269), we see that the right-hand side of Eq. (5.268) represents the Gibbs free-energy change ΔG° referred to a given temperature and reaction under standard conditions. Thus, Eq. (5.268) may be given in the form:

$$\Delta G^\circ = -RT \ln K_p \tag{5.270}$$

And since ΔG is equal to the maximum useful work with the opposite sign, then it follows that

$$W^\circ_{p,\,\max} = RT \ln K_p \tag{5.271}$$

The superscript in W°_p signifies that the maximum useful work refers to the reaction carried out under standard conditions.

Comparing Eqs. (5.270) and (5.271) with relation (5.146), we see that they are completely identical. Thus, the method of characteristic functions and the method based on the use of the entropy alone lead to the same results.

The introduction of the functions F and G has nevertheless been fruitful. First, these functions simplify the investigation of equilibria, i.e., they are convenient in practice. Second, the isothermal changes of these functions are quantities that can, in principle, be directly determined experimentally; these quantities are the maximum work (v = const) and the maximum useful work (p = const).

For example, the construction of a galvanic cell on the basis of a given chemical reaction and the measurement of its electromotive force (emf) give the maximum work of the reaction and, hence, ΔG or ΔF. The determination of the standard entropies of the individual participants in the reaction is, however, a considerably more formidable task. At the same time, the temperature dependence of ΔG and ΔF determined from the temperature dependence of the emf is *in essence the entropy change in the reaction.*

Chapter 6

Elements of Statistical Thermodynamics

6.1. Entropy and Randomness of the State of a System

The second law of thermodynamics affirms the existence of a certain property of a system, S, associated with heat exchange and a temperature at which this heat exchange takes place:

$$dS \geqslant \frac{\delta Q}{T} \tag{6.1}$$

or, for an isolated system in the absence of heat exchange:

$$dS \geqslant 0 \tag{6.2}$$

As we already know, this property denoted by S is called the entropy. Relations (6.1) and (6.2), which were derived by Clausius, are a mathematical expression of the second law of thermodynamics. These expressions specify that an increase in entropy is either equal to the reduced heat for equilibrium (reversible) processes or greater than the reduced heat for non-equilibrium (irreversible) processes.

Thus, the entropy is a property associated, on the one hand, with heat exchange and, on the other, with irreversibility. In this lies the dual nature of the entropy, a feature which undoubtedly makes it difficult, at the very outset, to grasp the physical meaning of this most important thermodynamic function. It appears, however, that it is exactly this duality that helps us to eventually understand the entropy, but not from the standpoint of the Clausius classical propositions but from the viewpoint of molecular statistics developed at a later time.

Deferring for a while a quantitative treatment of the problem, we should note here that the dual nature of the entropy can easily be understood if we resort to the concepts of the atomic-molecular structure of matter and consider the state of the system from the standpoint of the order-disorder of the motion or state of its constituent particles.

As an example of, so to say, the ideal orderliness of molecular structure may be cited a well-developed crystal of a pure substance (say, of a metal) at a temperature close to absolute zero. As known, the atoms (or molecules) in such a crystal are arranged at certain crystal-lattice points, near which they perform identical vibrational motions with the so-called *zero-point energy*. According to Planck (the third law of thermodynamics), the entropy of such a crystal equals zero. The ideal order is disturbed if the body is heated by absorbing heat. On moderate heating this results in the appearance of an ever increasing number of particles, which vibrate with different energies. The mean position of particles at lattice points is, however, retained. When the order is disturbed (or the disorder increases) under the influence of heat, the entropy is increased:

$$\Delta S = \int_0^T C \frac{dT}{T} \tag{6.3}$$

where C is the heat capacity.

The phase transitions solid ⇌ liquid and liquid ⇌ vapour, which are associated with the breakdown of the crystalline structure (melting) and with the formation, during the vaporization, of a system of weakly interacting and randomly moving particles, are accompanied by the isothermal absorption of heat and a sharp increase in entropy of the substance:

$$\Delta S_{\mathrm{m}} = \frac{\Delta H_{\mathrm{m}}}{T_{\mathrm{m}}} \quad \text{and} \quad \Delta S_{\mathrm{vapn}} = \frac{\Delta H_{\mathrm{vapn}}}{T_{\mathrm{vapn}}} \tag{6.4}$$

The value of ΔS is particularly high in the latter case, i.e., during the formation of the most disordered, chaotic state of aggregation—the vapour or gaseous state.

Thus, there is a certain parallelism between the absorption of heat by the system, the increase in the disorder of its molecular structure and the increase in entropy. All the processes described above could be made to proceed reversibly under equilibrium conditions and therefore relation (6.1) could be used for them with an equality sign.

But, according to relation (6.2), the increase in entropy of the system is also possible without any heat exchange under the conditions of a non-equilibrium process. Suppose, for example, that in an isolated system there is a mechanism incorporating a compressed ("wound") spring and a device that releases it at a specified moment. In general, the compressed spring would be able to perform work—for example, would compress another spring or some other thing and in this case, under the conditions of complete equilibrium, the entropy of the system would remain constant [the equality sign in relation (6.2)]. But the simply released spring uncoils irreversibly, without performing work. The potential elastic energy stored in the spring—the energy of the ordered state—is transformed to the energy of the random motion of molecules, i.e., the system is heated. In such a non-equilibrium process the disorder of the molecular state of the system also increases and so does its entropy, but this time no heat is absorbed from the surroundings.

Let us consider, as a further example, an electric storage battery shunted automatically in an isolated system with resistance. In this case, the organized and directed energy of the storage battery, which could, in principle, do work (for example, it could compress a spring), is transformed into Joule heat. The disorder of the molecular state of the system increases and so does the entropy of the system.

Many similar examples could be cited; they all show that in any non-equilibrium (irreversible) process any organized form of energy (capable, generally speaking, of being converted quantitatively, by way of performing work, into another, also organized form) is transformed to the disordered energy of the random thermal motion of molecules. In other words, in any such process the molecular chaos and, hence, the disorder of the molecular state of the system, increases.

Thus, the entropy of the system increases in parallel with the increase of the chaos or "mixtupness" of its molecular state, irrespective of whether this disorder is associated with the absorption of heat or with the conversion of the organized energy into heat. Hence, the entropy may be treated, from the qualitative standpoint, as a measure of the disorder ("mixtupness") of the molecular state of the system. Thus, one of the basic thermodynamic properties of a molecular system—its entropy—is found to be associated with the microscopic characteristics of the constituent particles of the system.

6.2. A Mechanical Description of a Molecular System

The qualitative concepts expounded in the preceding section are quantitatively developed by *statistical thermodynamics*, which is a part of a more general branch of science known as *statistical mechanics*. The basic principles of statistical mechanics were developed during the latter part of the nineteenth century by Boltzmann in Germany, Maxwell in England, and Willard Gibbs in the United States.

As we already know, in thermodynamics the state of a system consisting of a single pure substance is quite uniquely defined in a general case by three independent variables. For example, by the number of moles n, the energy U, and the volume v. From the microscopic standpoint, however, such a system, say 1 mole of a substance, contains about 10^{24} separately (to a certain extent) existing individual molecules. Statistical mechanics is concerned with the description of the state of each particle by specifying its coordinates and the nature of the motion performed. Here it is assumed that the molecular motion is described by the laws of classical mechanics which are used in the form of *Hamilton's canonical equations of motion*:

$$\frac{\partial q_i}{\partial t} = \dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \frac{\partial p_i}{\partial t} = \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{6.5}$$

where H is the Hamiltonian function which expresses the total energy for conservative systems; q is the coordinate; p is the momentum; t is the time. In this connection, it may be noted that, although the behaviour of a particle of atomic (or subatomic) dimensions must be described, strictly speaking, by the laws of quantum mechanics, it is nevertheless possible to obtain correct results in many cases, using the laws of classical mechanics. For instance, the translational motion of molecules and also their rotation and intramolecular vibrations can be described within the framework of classical mechanics with an accuracy sufficient in a number of cases. A classical description supplemented with the required detailing made by means of quantum mechanics is most successful. We shall deal with this detailing at a later time. At this point we shall be concerned with a consideration of the classical approach.

In a general case, the position of a particle in space, say a polyatomic molecule, must be described by f generalized coordinates:

$$q_1(t),\ q_2(t),\ \ldots,\ q_f(t) \tag{6.6}$$

which depend on time. For example, for a molecule consisting of m atoms one must make use of $3m$ *Cartesian* (or any other) coordinates in order to describe the system mechanically. Associated with f coordinates are the corresponding f conjugate momenta, which are also time-dependent:

$$p_1(t),\ p_2(t),\ \ldots,\ p_f(t) \tag{6.7}$$

Thus, for a precise description of the "state" of a particle it is necessary to specify the instantaneous values of altogether $2f$ variables.

For further treatment it is useful to imagine a multi-dimensional space with $2f$ coordinates which may be called the phase μ-space.* A point in such a phase space will represent the "state" of a particle at time t, and the change of this state in time will be uniquely described, by virtue of the determinacy of the laws of classical mechanics, by a certain trajectory of the motion of the representative point. For example, we can represent, on a plane, the phase space for $f = 1$ and the corresponding path, which defines the time function:

$$q = q(t) \text{ and } p = p(t) \tag{6.8}$$

As an example of a system with $f = 1$, let us consider a linear harmonic oscillator having the total energy ε. As known, in this case

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* To memorize: the μ-space (the *mu*-space) is the phase space for a single *mo*lecule.

$$\varepsilon = \frac{p^2}{2m} + k\frac{q^2}{2} = (T+U) \tag{6.9}$$

where m is the mass of the vibrating particle; q is the displacement from the equilibrium position; k is the force constant of the quasi-elastic force (Hooke's law). As can be seen from relation (6.9), the phase trajectory will be depicted in this case by an ellipse* (Fig. 6.1).

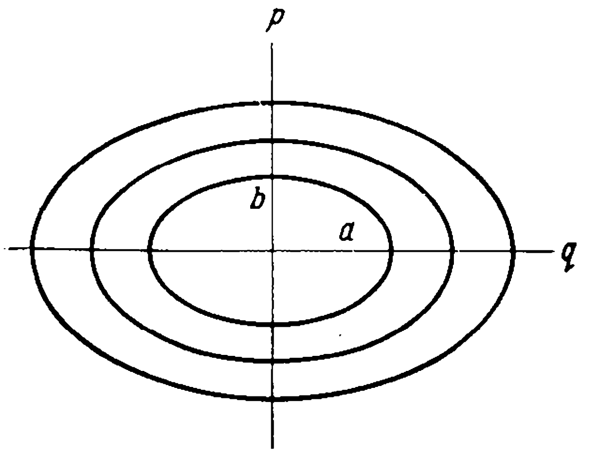

Fig. 6.1. Phase trajectories for a harmonic oscillator (the area of the ellipse $\int pdq = \pi ab = 2\pi\varepsilon\sqrt{m/k}$).

For a more complex system, say a gas containing N polyatomic molecules, the procedure is essentially the same. The only difference is that the phase space has now $2Nf$ dimensions and is called the gamma-space (the γ-space).** A point in such a space will represent the instantaneous state of the whole system, i.e., will provide a detailed description of each of its constituent particles—the precise values of all the $2Nf$ variables. Accordingly, the path of such a representative point will describe the progress of the system concerned in time. In this case, the path is determined by $2Nf$ equations of the form of Eqs. (6.8), i.e.,

$$q_i = q\,(t);\; p_i = p\,(t)\; (i = 1,\ 2,\ 3,\ \ldots,\ Nf) \tag{6.10}$$

which in turn are defined by Hamilton's equations of motion:

$$\dot{q}_i = \frac{\partial H}{\partial p_i};\quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (i = 1,\ 2,\ 3,\ \ldots,\ Nf) \tag{6.11}$$

in conjunctions with $2Nf$ initial conditions $q_i\,(0)$ and $p_i\,(0)$. Here the Hamiltonian function H depends on all $2Nf$ variables. Further in the text we shall make use of the following abbreviated notation for this dependence:

$$H\,(p,\ q) \tag{6.12}$$

---

* We divide both sides of (6.9) by ε:

$$\frac{p^2}{2m\varepsilon} + \frac{q^2}{2\frac{\varepsilon}{k}} = 1$$

Introducing the notations $a = \sqrt{2m\varepsilon}$ and $b = \sqrt{2\varepsilon/k}$, we obtain the ellipse equation $p^2/a^2 + q^2/b^2 = 1$.

** To memorize: the γ-space (the gamma-space) is the phase space for the assembly of molecules (the entire gas).

It should be noted that since the laws of classical mechanics are determinative*, the trajectory emerging from a given point is unambiguously defined. Strictly speaking, this leads to the statement that *the trajectory in a phase space cannot intersect itself.*

6.3. Microstates and Gibbs Ensembles

The state of a system defined in thermodynamics by the properties of the system—its volume, pressure and temperature, will be called here the *macrostate* of the system. We shall distinguish between the macrostate and the *microstate*, which is characterized by the instantaneous values of all $2f$ time-dependent variables for all N constituent particles of the system.

If the system is at equilibrium, then its macrostate does not change in time. The microscopic variables characterizing individual particles can, however, change continuously but in such a way that the macrostate remains unaltered. There must therefore exist, from the classical standpoint, an infinite set of microscopic states, which are consistent with the macroscopic characteristic of the thermodynamic system.

For a study of the statistical behaviour of thermodynamic systems Gibbs proposed the *method of ensembles.* According to Gibbs, an ensemble is a sufficiently large set of microstates, which are compatible with a particular thermodynamic or macroscopic state. In other words, an ensemble may be visualized as a tremendously large collection (tending to infinity in the limit) of analogous thermodynamic systems, each having the same characteristics from a thermodynamic or macroscopic point of view but each in a different stage of development, i.e., in a different microstate.

Depending on the task set forth, use is made of various ensembles, which correspond to the various constraints imposed on the thermodynamic system. The most important ensembles are those described below.

The microcanonical ensemble (or assembly) corresponds to an isolated system, which cannot exchange either matter or energy with the surroundings. It is defined to have constant v, U, N (or the series N_1, N_2, . . ., if the system is a multicomponent one).

A canonical ensemble corresponds to a closed isothermal system which is characterized by the values of v, N, and T. Such a system is in thermal equilibrium and can exchange energy with the surroundings. A canonical ensemble has been found to be most suitable for the purposes of statistical thermodynamics.

The two ensembles described are collectively referred to as *petit canonical ensembles.*

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* In the subsequent discussion we shall dispense with this strict determinacy.

The third type of ensemble, known as the *grand canonical ensemble*, corresponds to an open isothermal system characterised by the constant volume v, temperature T and average number of particles (the constraint of constant average number of particles in the ensemble is equivalent to a constant chemical potential μ). The grand canonical ensemble is in both thermal and material equilibrium with the surroundings and can exchange both energy and matter.

The evolution of the microscopic dynamic state of each replica system in petit canonical ensembles will be described by the trajectory of its representative point in the $2Nf$-dimensional phase space. If the same space contains the representative points of all the other systems of the ensemble, there will appear, as it were, a cloud of moving representative points. The instantaneous density of the cloud at a given point can be defined by the distribution function

$$\rho\,(q_1, \ldots, q_f, p_1, \ldots, p_f, t) \tag{6.13}$$

or, in an abbreviated notation, $\rho\,(q, p, t)$. The distribution function is normalized as follows:

$$\int \ldots \int dq_1 \ldots dp_f \rho\,(q, p, t) = 1 \tag{6.14}$$

The quantity ρ should be looked upon as the *fraction* of the total number of systems in the ensemble per unit *hypervolume* of the phase space in the region of the point $q_1 \ldots p_f$ at time t. The integrand in Eq. (6.14) is also the fraction of systems but in the hypervolume element $dq_1 \ldots dp_f$. Evidently, ρ also expresses the probability of the representative point of a randomly chosen system in the ensemble being in this or that unit volume of the phase hyperspace.

6.4. Liouville's Theorem

The movement of a "cloud" of points in the phase space is determined by the laws of mechanics, i.e., by Hamilton's equations of motion (6.11), which have continuous solutions. From this it follows that adjacent representative points belong to adjacent trajectories. The hypervolume elements defined by the content of the various numbers of points are deformed continuously (in the sense of the continuity of functions) during the motion in time. In this section we shall show that the hypervolume occupied by these points nevertheless remains constant. This is equivalent to the statement that the probability distribution may be depicted as an incompressible liquid.

As has already been said, phase trajectories are continuous curves—they cannot be started or broken. In other words, representative points can be neither created nor destroyed, i.e., the "probability liquid" is indestructible. Therefore, within each stationary hypervolume element $\Delta\omega$ the rate of increase of the number of representative points must be exactly equal to the total number of points leaving $\Delta\omega$. If $\Delta\omega$ is diminished infinitely, we shall obtain the analogue of the equation for the flow of an indestructible liquid, i.e.,

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho\bar{v}) = 0 \tag{6.15}$$

where $\bar{v}$ is the flow-rate vector.

In a three-dimensional space the term with divergence (the vector divergence) has the form

$$\operatorname{div}(\rho\bar{v}) = \frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z) \tag{6.16}$$

On the basis of the identity (6.16) we write the generalized equations (6.15) in extended form for $2Nf$ measurements:

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{Nf} \left[\frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i)\right] = 0 \tag{6.17}$$

Differentiating the products in Eq. (6.17), we obtain

$$\frac{\partial \rho}{\partial t} + \sum \left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] + \rho \sum \left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right] = 0 \tag{6.18}$$

Using Hamilton's equations (6.11) and noting that for continuous functions the order of differentiation is immaterial, we become convinced that the second sum in (6.18) is equal to zero. Indeed, each term of this sum assumes the following form in accordance with Eqs. (6.5):

$$\frac{\partial^2 H}{\partial p_i \partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i}$$

But they have different signs. Further, since ρ is considered to be a function of q_i, p_i and t, the remaining terms in (6.18) are a total derivative with respect to time, i.e.,

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{Nf} \left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] = 0 \tag{6.19}$$

which can also be obtained by dividing the total differential of the function ρ (q, p, t) by dt.

It is worthwhile to pay attention to the difference between the derivatives $\partial\rho/\partial t$ and $d\rho/dt$. The first is the change of the probability density in time in the neighbourhood of the stationary point $q_i p_i$ of the phase space, while the total derivative $d\rho/dt$ represents the corresponding change in the vicinity of the moving representative point, which follows its trajectory in accordance with Hamilton's equations of motion.

Taking cognizance of Eqs. (6.18) and (6.19), we arrive at *Liouville's theorem* (1838):

$$\frac{d\rho}{dt}=0 \tag{6.20}$$

which states that *the density of representative points remains constant in the neighbourhood of a representative point moving in a phase space.* Therefore, as stated at the beginning of this section, the hypervolume element $\Delta\omega$ can change its shape in the course of time but it cannot be expanded or compressed.

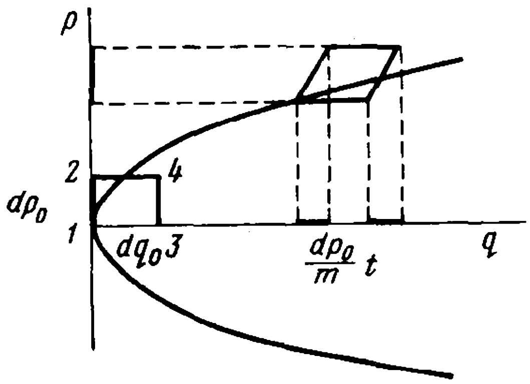

Fig. 6.2. Illustrating Liouville's theorem (the phase space for falling material points remains constant).

Consider an example associated with the fall of a material point of mass m in the field of earth gravity. The momentum and coordinate of the point will be expressed by the following functions:

$$p=mgt, \quad q=\frac{1}{2}gt^2 \tag{6.21}$$

where g is the acceleration due to gravity.

To define the phase trajectory, we eliminate time from (6.21) and obtain the equation:

$$q=\frac{p^2}{2mg} \tag{6.22}$$

Hence, in this case the phase trajectory is a parabola (Fig. 6.2). Suppose that, apart from point *1*, we are also interested in the motion of three other points, which are moving in the same gravitational field but differ from point *1* by other initial values of p_0 and q_0, as shown in Table 6.1.

TABLE 6.1

Points	p_0	q_0	p	q
1	0	0	mgt	$\frac{1}{2}gt^2$
2	dp_0	0	$mgt+dp_0$	$\frac{1}{2}gt^2+\frac{dp_0}{m}t$
3	0	dq_0	mgt	$\frac{1}{2}gt^2+dq_0$
4	dp_0	dq_0	$mgt+dp_0$	$\frac{1}{2}gt^2+\frac{dp_0}{m}t+dq_0$

From the data given in Table 6.1 and Fig. 6.2 it is seen that the four points of interest, which formed on the phase plane p-q a rectangle dp_0dq_0 at the beginning of their motion, change their relative position with time. However, the points *1* and *3* and also the points *2* and *4* will be at all times at the same height and the distance between them, dq_0, will remain unchanged. At the same time the upper side of the quadrangle *1342* is moving in parallel to the axis q more rapidly than the lower side because the points *2* and *4* have an initial momentum dp_0. Therefore, the orthogonal quadrangle changes with time to a parallelogram. Nevertheless, the area of the figure formed by the four points on the phase plane remains unchanged even during the motion, as required by Liouville's theorem.

6.5. The Ergodic Hypothesis and the Basic Postulates of Classical Statistical Mechanics

According to Liouville's theorem, all regions of a phase space through which the point representing the evolution of a system passes are defined to have the same density. This proposition, which has been shown to follow from the laws of mechanics, should be supplemented, for the basic principles of statistical mechanics to be formulated, with the *ergodic hypothesis*, which was originally advanced by Boltzmann and Maxwell: *the representative point of an isolated system (v, N and U are constant) passes through all accessible (i.e., consistent with the specified conditions) points of the phase space before it returns to its initial position.*

In other words, after the lapse of a very long period of time a mechanical system will return to its initial state after it has passed through all the other accessible states, the accessibility in this case being restricted by the observation of the law of conservation of energy*:

$$U \text{ (or } E) = H(q, p) = \text{const} \tag{6.23}$$

The ergodic hypothesis, which was termed by Maxwell the principle of the path continuity, cannot be proved, for which reason it is called a hypothesis. Furthermore, Ehrenfest and Afanasieva-Ehrenfest suggested that in the formulation of this hypothesis the phrase "before it returns to its initial position" be replaced by "before it eventually approaches as closely as possible each of the accessible points of the phase space". The need for this correction is associated also with the existence of dynamic systems whose representative points never enter the accessible regions of their phase space. Such systems may be called *nonergodic*: an example is a planetary system in which the planets will evidently be always in the plane of the ecliptic, though the orbits that are located, say, in a perpendicular plane, are energetically quite "accessible". Thus, the ergodic hypothesis or the quasi-ergodic hypothesis (according to the Ehrenfests) imposes certain constraints on systems subject to a study from the standpoint of statistical mechanics: such systems must be ergodic. As has been found out, ergodic systems consist of a sufficiently large number of interacting particles.

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* For conservative system under consideration the Hamiltonian function expresses the total energy of the system.

The ergodic hypothesis in conjunction with Liouville's theorem leads to the basic propositions of statistical mechanics which are sometimes postulated. The first postulate is the principle of equal a priori probabilities: *In an isolated system all the possible quantum states consistent with specified values of the number of particles, the volume and the energy are all equally probable.*

The second postulate is the theorem of averages: *The time average of the energy or pressure (or other mechanical property) is equal to the average of these properties for the ensemble as* $\eta \to \infty$.

The first postulate stems from the statement that the representative point which moves, in accordance with Liouville's theorem, in a medium of constant density ρ, passes through every point in the accessible regions of the phase space in agreement with the ergodic hypothesis. In other words, for an ensemble, which is an isolated thermodynamic system, i.e., the microcanonical ensemble, the representative points are distributed uniformly in an accessible phase space.

The second principle is based on the following reasoning: each system in the ensemble will come, in the course of a sufficiently long period of time, to the state of each other member of the ensemble in accordance with the ergodic hypothesis. Therefore, the time averaging for each system taken separately leads to the same result as does a conceivable instantaneous averaging over the entire ensemble. It is precisely the theorem of averages that allows one to establish the exact relationships between the thermodynamic variables (the properties of the system) and the mechanical microscopic characteristics. Thus, each thermodynamic property θ, say, the pressure, energy, or entropy, is determined as the time average of some dynamic variable $\theta\,(p,\ q)$. Hence, using a bar for the time average, we have:

$$\theta = \overline{\theta\,[q\,(t),\ p\,(t)]} \tag{6.24}$$

For example, the pressure of a gas corresponds to the average rate of transport of momentum per unit surface area of the vessel.

The time average of a dynamic variable is given by the expression

$$\overline{\theta\,(q,\ p)} = \frac{1}{\tau}\int_0^\tau \theta\,[q\,(t),\ p\,(t)]\,dt \tag{6.25}$$

where τ is a period of time long enough to permit a physically meaningful measurement of the thermodynamic property concerned. The ensemble average is given by a different relation:

$$|\,\theta(q,\ p)\,| = \int \ldots \int \theta(q,\ p)\,\rho(q,\ p,\ t)\,dq_1 \ldots dq_f\,dp_1 \ldots dp_f$$

and is the average of θ over all the systems in the ensemble at a certain time. Using the notations introduced, we may write the theorem of averages as follows:

$$\overline{\theta(q,\ p)} = |\,\theta(q,\ p)\,| \tag{6.26}$$

Here it should be kept in mind that equality (6.26) is the basic expression which relates the mechanical description of the system with its thermodynamic description and is valid only for ergodic systems.*

6.6. Calculation of Microstates According to Boltzmann

The simplest way for describing the mechanical state of systems consisting of a large number of identical molecules, for example, 1 mole of any chemically pure gas, is to use the $2f$-dimensional phase μ-space if f is the number of degrees of freedom of a molecule (see Sec. 6.2). As has already been said, a point in such a space will precisely define the coordinates $(q_1 \ldots q_f)$ and momenta $(p_1 \ldots p_f)$ of a given single molecule. The number of dimensions in the γ-space, which is used to describe the state of the system as a whole, will be N times larger, i.e., will be equal to $2Nf$, if N is the number of molecules in the system. If there are no (strong) forces of interaction between the molecules**, the γ-space of the system may be visualized as a set of individual μ-spaces. The location of a point in the γ-space of the system describes the position of the representative point of each molecule in its own μ-space and specifies the state (microstate) of the system as a whole. It is also obvious that the instantaneous microstate of a system of N molecules will be characterized by a distribution of representative points in μ-spaces. As has been said earlier, from the classical standpoint an infinitely large number of microstates will correspond to a given equilibrium macrostate, since the molecules are constantly moving and colliding with each other, exchanging their momenta.

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* The equivalence of time and ensemble averages can be proved for so-called metrically transitive systems, i.e., systems whose phase trajectories will pass, if only one waits long enough, through every point on the energy surface (volume). In the opposite case of metrically non-transitive systems the energy surface is divided into sections, and the trajectory of the representative point is confined to lie in only one section. A metrically transitive system is ergodic (quasi-ergodic). For a deeper understanding of this rather sophisticated subject the reader is referred to specialized treatises.

** But the molecules are still expected to interact with one another to a certain extent, otherwise no energy exchange will be possible between the molecules and no equilibrium distribution will be attained—a system whose molecules do not interact at all will not be ergodic.

It is essential to restrict the number of microstates so as to prevent it from becoming infinitely large. To do this, it will suffice to agree to define the coordinates and momenta of particles not with absolute accuracy but within the ranges q_i to $q_i + dq_i$ and p_i to $p_i + dp_i$. In other words, to render a set of macrostates countable, the phase μ-space is split into elementary cells of the volume*

$$\Delta\omega = dq_1 \dots dq_f \, dp_1 \dots dp_f$$

and the state of a molecule is assumed to be sufficiently well defined if the corresponding representative point is in a given elementary cell.

In Boltzmann classical statistics, the macrostate of a system, say, any ideal gas, is defined by the number of representative points of molecules in various cells of the phase space. In order to define microstates in Boltzmann statistics it is also necessary to specify the representative points of which molecules are in which cell. In other words, molecules are considered to be distinguishable and the interchange of places by two molecules which are in different cells will give rise to a new microstate, the macrostate remaining unaltered.

Thus, the number of microstates corresponding to a given macrostate can be calculated if we find the number of permutations of representative points in the cells.

Suppose a system consists of N molecules and to its macrostate there correspond N_1 representative points in the first cell, N_2 points in the second cell and so on, and in a general case N_i points in the ith cell. Since the interchanges of places within a cell are disregarded (they do not produce new microstates), the number of microstates is found as the number of inversions of order with recurrences:

$$G = \frac{N!}{N_1! \, N_2! \dots N_i!} \tag{6.27}$$

We shall illustrate the method by an example. Let us agree to consider the distribution of molecules only in an ordinary three-dimensional space. We shall confine ourselves to six molecules and three cells:

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* In quantum statistics, using Heisenberg's uncertainty principle $dqdp \geqslant h$, where h is Planck's constant (more exactly, divided by 2π), it is assumed that an elementary cell (localized statistical element) $\Delta\omega = h^f$. In classical statistics, the volume of an elementary cell remains undetermined.

I	1, 2, 3 4, 5, 6		
II	1, 3	4, 6	5, 2

The above diagram shows two "macrostates": macrostate I in which all the molecules are in one cell and macrostate II in which the molecules are distributed uniformly among all the cells. The number of "microstates" corresponding to the first "macrostate" is equal to unity: all the molecules are in the first cell and the inversions within the cell are disregarded. For the second macrostate we calculate G from formula (6.27):

$$G = \frac{6!}{2!2!2!} = 90$$

that is, the second macrostate can be obtained in 90 different ways according to classical statistics.

Even from the most general considerations it follows that the second state must be realized much more frequently. The number G calculated by the method described above by means of formula (6.27) is also called the *number of complexions.*

6.7. Thermodynamic Probability and Entropy

From the principle of equal a priori probabilities (see Sec. 6.5) it follows that all the microstates of a system compatible with the specified conditions (for example, with the condition of constant energy) are mathematically equally probable. At first glance one might think that this hypothesis cannot correspond to reality. Indeed, let us compare two microstates of one mole of a gas. Suppose that in one state the gas mole occupies the entire volume of the vessel, say 10 litres, and that its molecules are in chaotic motion. We shall assume that this microstate corresponds to an equilibrium macrostate. In the other microstate all the molecules have accumulated in a volume of 1 cm^3 and are moving in parallel to one another. It is really difficult to visualize a spontaneous transition of the first equilibrium state to the second nonequilibrium state. But the principle of equal a priori probabilities leads to correct consequences and is evidently valid. The point is how often the various microstates are encountered.

To understand the essence of the matter it is useful to resort to a pack of 52 cards. Imagine also a machine that shuffles the whole pack once per second. As a result of this procedure, there may obtain any distribution of cards, including the ordered arrangement by seniority and by suits. The probabilities of distributions (microstates) are equal. But there is only one ordered arrangement, while the number of disordered arrangements is

$$52! \approx 10^{37}$$

With the frequency of change of combinations being 1 $\sec^{-1}$ each of the combinations, including the ordered one, will be encountered once in 10^{30} years. Hence, though all the arrangements are equally probable, the appearance of the ordered arrangement is extremely improbable since it is the only one out of 10^{37} various arrangements.

Likewise, we could also compare the recurrence or waiting time of the above-indicated microstates of a gas with the only difference that for a non-equilibrium state it is so enormously great that it is difficult to express it with the aid of ordinary methods of writing numbers; we may write, say, the number 10^{30} raised to the power of 10^{30}, but this will get us nowhere.

The concept of microstates and of their equal probabilities and also the fact that to different macrostates there may correspond different numbers of microstates leads to the idea of the thermodynamic probability of a state (a macrostate):

$$W = \text{const}\, G \tag{6.28}$$

that is, the thermodynamic probability of a state is proportional to the number of microstates corresponding to a given macrostate. Furthermore, we may assume the proportionality factor to be equal to unity and regard W as the relative probability, i.e., the probability of any particular state with respect to the probability of some reference state.

The quantity W may also be regarded as the numerator of the mathematical probability, the denominator of which is the number of all microstates conceivable for a given system of microstates compatible with the laws of conservation. Thus,

$$W = G \geqslant 1 \tag{6.29}$$

the value of W being very large for ordinary molecular systems.

The statistical significance of the second law of thermodynamics consists, according to Boltzmann, in that an isolated system undergoes evolution predominantly in the direction of a greater thermodynamic probability. To put it in a different way, the second law of thermodynamics has no absolute validity as compared with the first law since the spontaneous formation of nonequilibrium states, say the self-compression of a gas, is not absolutely impossible. But the thermodynamic probability of such states is very low: they are represented by a small number of microstates and can therefore be realized very rarely.

As can be shown, the thermodynamic probability of a state of equilibrium for ordinary molecular systems, say 1 mole of a gas, is found to be many times greater than the sum of the thermodynamic probabilities of all possible nonequilibrium states:

$$W_{(\text{eq. state})} \gg \sum_{\text{all}} W_{(\text{noneq. states})}$$

Thus, an isolated system undergoes evolution to the side of *increasing* thermodynamic probability, and the equilibrium state corresponds to the greatest, maximum value of W. But it is exactly in this manner that the entropy of an isolated system is changed. Therefore, these quantities must be interrelated, i.e.,

$$S = f(W) \tag{6.30}$$

To establish the form of this function, let us consider two independent systems with the probabilities of states W_1 and W_2. If a new composite system is built up of these two systems, its thermodynamic probability will be given, according to the theorem of multiplication of probabilities, by the product $W = W_1W_2$. The entropies of the systems taken separately are $S_1 = f(W_1)$ and $S_2 = f(W_2)$ in conformity with Eq. (6.30), and the entropy of the complex system equals the sum of these entropies since S is an extensive, additive property of the system: $S = S_1 + S_2$ or

$$f(W) = f(W_1) + f(W_2) \tag{6.31}$$

Likewise, according to Eq. (6.30), $f(W_1W_2) = f(W_1) + f(W_2)$. This expression is differentiated first with respect to W_1: $W_2f'(W_1W_2) = f'(W_1)$ and then with respect to W_2 : $f'(W_1W_2) + W_1W_2f''(W_1W_2) = 0$ or $f'(W) + Wf''(W) = 0$. We rewrite the last equation in the form:

$$1 + W\frac{f''(W)}{f'(W)} = 0$$

or

$$\frac{f''(W)}{f'(W)}dW = -\frac{dW}{W}$$

Integration yields:

$$\ln f'(W) = -\ln W + \ln \mathrm{k} = \ln\frac{\mathrm{k}}{W}$$

where ln k is the integration constant.

Since with the logarithms being equal the logarithmic expressions are also equal, we may write down:

$$f'(W) = \frac{\mathrm{k}}{W}$$

or, multiplying by dW,

$$f'(W)\,dW = \mathrm{k}\frac{dW}{W}$$

Integrating once again, we obtain:

$$f(W) = \mathrm{k} \ln W + \text{const} \quad \text{or} \quad S = \mathrm{k} \ln W + \text{const}$$

But, by virtue of Eq. (6.31), the integration constant here is equal to zero. Therefore, we may finally write the equation

$$S = \mathrm{k} \ln W \tag{6.32}$$

which establishes a relationship between the entropy and the thermodynamic probability and is known as the *Boltzmann equation.* It was first written in this form by Planck in 1900. This equation is the fundamental equation of statistical thermodynamics.*

In Eq. (6.32) the constant k is, strictly speaking, arbitrary but we are interested in choosing this constant so that the entropy defined by this equation would coincide with the ordinary, so to say, thermodynamic entropy of the second law. To this end, let us consider the isothermal expansion of an ideal gas from volume v_1 to volume v_2. According to Eq. (6.32), the entropy change will be given by

$$\Delta S = \mathrm{k} \ln \frac{W_2}{W_1} \tag{6.33}$$

The probabilities of one molecule residing in the final volume v_2 or in the initial volume v_1 are interrelated as the volumes themselves, i.e., v_2/v_1. If there are two molecules, the ratio of the probabilities will be equal to $(v_2/v_1)^2$ and so on. For a mole of a gas

$$\frac{W_2}{W_1} = \left(\frac{v_2}{v_1}\right)^{N_A}$$

where N_A is Avogadro's number equal to 6.0220×10^{23}. Thus, according to Eq. (6.33), the entropy change is given by

$$\Delta S = \mathrm{k} N_A \ln \frac{v_2}{v_1}$$

But, on the other hand, the change in entropy of one mole of an ideal gas upon isothermal expansion from v_1 to v_2 is given by the well-known formula

$$\Delta S = R \ln \frac{v_2}{v_1}$$

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* While Eq. (6.32) is missing in the works of Boltzmann, they contain, however, the famous *H-theorem.* The function H, which decreases in isolated systems, is equal to the entropy with a minus sign. Planck gave only the interpretation of Boltzmann's H-theorem. The enormous importance of Boltzmann's works, which made a breach in Clausius's pessimism ("the entropy of the Universe tends to a maximum"), is embodied in the brief epitaph on Boltzmann's gravestone in the beautiful Vienna: $\boxed{S = \mathrm{k} \ln W.}$

Therefore, for the *statistical entropy to coincide with the thermodynamic* entropy it is necessary to put:

$$k = R/N_A = 1.38066 \times 10^{-16} \text{ erg/deg}$$

The quantity defined in this way is called the *Boltzmann constant*. It is one of the universal physical constants.

It is appropriate now to return to the question of a qualitative treatment of the entropy of the system as a measure of the disorder of its state (Sec. 6.1). Proceeding from the concepts expounded in this section, a quantitative measure of disorder is the thermodynamic probability or the number of microstates. From this standpoint, the changes that occur in the system due to the absorption of heat—through heating, melting, evaporation, etc.—may also be regarded as being associated with an increase in W, i.e., with an increase in the number of microstates corresponding to a new macrostate, say a liquid as compared with a crystal. Hence, the Boltzmann equation can also be used to calculate the change in entropy of the system during the course of processes involving heat exchange.

In connection with the statistical interpretation of the entropy some attention should be focused on the question of the so-called heat death of the Universe. One of the founders of classical thermodynamics, Clausius, gave the following formulations of the first and second laws of thermodynamics: (1) The energy of the Universe is constant. (2) The entropy of the Universe tends to a maximum.

Whereas the first formulation does not cause serious objections because of the absence of information about departures from the law of conservation of energy and of the recognition that it is an absolute regularity, the second formulation is looked upon in quite a different manner. Extending the law of entropy increase, which has been established for spontaneous processes that occur in an isolated system, to the Universe, Clausius arrives at the inevitable conclusion that the Universe tends to a state of thermal equilibrium—the "heat death"—as soon as the temperatures, pressures and so on are balanced and, as a consequence of the established equilibrium, any processes will be stopped. This pessimistic conclusion from the second law of thermodynamics has been repeatedly the source of idealistic and theological speculations* since the recognition of the inevitable end of the Universe leads logically to the assumption of its origin, of the first impact and, finally, of the act of creation.

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* Thus, not very long ago (November, 1951) the Pope Pius XII wrote in his message to the Vatican Academy of Sciences: "According to the entropy law enunciated by Rudolf Clausius, spontaneous processes that occur in nature always involve a decrease in the free energy. In a closed system this must inevitably lead to the cessation of all macroscopic-scale processes. This inevitable fate predicted for the Universe ... serves as an eloquent confirmation of the existence of the Supreme Being".

Considering the above formulation of the second law and the inferences made from it to be quite incorrect from the viewpoint of materialistic philosophy, we should nevertheless note that the physical solution of the problem has not been completed up to the present time. We shall only outline some of the possible ways for its solution. The works of Boltzmann* have shown that the second law is not an absolute principle and has a quite distinct restriction, so to say, from "downward". This is a statistical law, which is applied on an average to systems consisting of a large number of particles. The application of the second law to an atom, a molecule, or systems consisting of a small number of these, is pointless. What has been said can be explained through a calculation of the probability or waiting time of the density fluctuation. Let us consider, as an example, 1 cm^3 of a gas under normal conditions. Is it possible that in this volume there will be accumulated an amount of gas corresponding to an increase in density, say. by 1 per cent? Yes, it is! Such an event, however, can hardly be repeated. It can be estimated by the waiting time which has been shown by calculations to be equal to $(10^{10})^{14}$ sec. The reader can convert these seconds to years, remembering that a year is equal to about 10^7 sec. But if the volume element is diminished to 2.5×10^{-5} cm^3, the waiting time will be reduced to one second. With even smaller volumes there are constantly very large fluctuations in the density. One should understand that for a system consisting of any large number of particles the process of self-compression or any other process involving a decrease in entropy is not absolutely impossible—it is hardly probable and therefore occurs seldom.

When turning to the cosmic scale, several questions arise. For example, what is the entropy of the Galaxy? In any event, it is not the sum of the entropies of its constituent parts—stars, nebulae or other formations. The Galaxy itself, while consisting of a very large number of stars (about 10^{11}), is a statistical (ergodic) system, which should perhaps be assigned a certain galactic super-entropy; we know nothing about the tendencies of the change in this entropy.

On the other hand, one may ask: Is not the Universe or a part of it, accessible to our observation, in a state resembling the state of thermal equilibrium? Thermal equilibrium does not in the least mean the complete absence of motion. For example, in a vessel containing a gas, which is in thermal equilibrium with the surroundings, the molecules themselves and the atoms in them are moving and the various acts of energy transfer are being performed, say, electron transitions brought about by collisions, etc. Besides, various fluctuations are possible, for example, density fluctuations. Any fluctuations are possible in the infinite and infinitely existing and, let us say, equilibrium Universe; and, taken by fantasy, we may assume that everything that is observable in the surveyable Universe is a *local* fluctuation. Other conceptions of the Universe have, however, been developed in the last few decades.

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* The Boltzmann H-theorem (1872).

In 1922 the Soviet scientist A. A. Fridman, based on the general theory of relativity, proposed a model of the non-stationary Universe. In 1929 the American scientist Hubble discovered the red shift in the spectra of the Galaxies. It consists of a displacement of lines in the spectra of distant galaxies toward longer wavelengths and, according to Doppler, increases with distance from the observer. This so-called cosmological red shift has been found to be proportional to the distance to an observable galaxy. In other words, the farther is the galaxy, the greater is the velocity with which it moves away. Hence the concept of the "scattering" of galaxies and of the expansion of the Universe.

Further development of the problem has led to the viewpoint that the Universe is a pulsating system.

The Universe has been expanding since an explosion that occurred about 10^{10} years ago. The expansion must reach a maximum in 3×10^{10} years, following which the Universe will begin to compress to a very small volume and enormous densities. This will be followed by an explosion and expansion will begin again. The entire cycle from the start of expansion to the end of compression must take about 10^{11} years according to the available estimates. The modern period, as may be seen, belongs to the initial stage of expansion.

Without delving into the discussion of the nature of the completeness of the concepts and inferences described above, we can nevertheless come to the conclusion that the scale and physical essence of cosmic phenomena are completely different from those of the restricted terrestrial observations, for which the second law of thermodynamics was enunciated.

The physical foundation for a different quality of cosmic-scale phenomena as compared with those observed in the laboratory perhaps consists in that the principal mode of interaction in outer space is the gravitation, which plays a secondary role in the case of small masses. For example, the force of gravitational interaction between a proton and an electron in the hydrogen atom is only 4×10^{-40} of the force of Coulomb interaction holding the electron in the atom. On the other hand, the force of gravity, as is believed, can reach such a magnitude in a cosmic object that the light cannot excel it and the object ceases to emit light—this phenomenon results from a gravitational collapse. In connection with what has been said above it is important to understand that the second law of thermodynamics is not an absolute principle and loses its meaning when applied to systems consisting of a small number of particles and also to systems of cosmic dimensions.

6.8. The Boltzmann Distribution Law

Many branches of physics and physical chemistry make use of the law that describes the distribution of molecules among their energy levels in an equilibrium molecular system. The use of this law is often helpful, even if the system is a non-equilibrium one but does not differ strongly from an equilibrium system. For example, the theory of chemical kinetics makes use, in a number of cases, of the concept of the formation of a certain intermediate product (or a transition state), which is relatively slowly converted into the final products. The concentration of such an intermediate therefore does not differ substantially from an equilibrium concentration and can be calculated, to a first approximation at least, by the methods of thermodynamics. In general, it is in this way that kinetics become related to thermodynamics.

In this connection, the methods of statistical thermodynamics which permit the calculation of the thermodynamic functions of a system consisting of a large number of molecules on the basis of the molecular characteristics obtained by spectroscopy, electron diffraction and other techniques, are important not only in the field of thermodynamics. They also play an important role in chemical kinetics and, in the first place, in the statistical calculation of the reaction rate (the theory of absolute reaction rates).

These methods are based on the law of distribution of molecules among the various energy levels which is known as the *Boltzmann distribution law*. To derive this law, suppose that the gaseous system under study consists of a very large number N of molecules. It has a specified total (internal) energy* U and occupies a constant volume v. Thus, from the thermodynamic viewpoint this is an isolated system (U = const and v = const).

We assume that all the molecules are chemically identical but may have different energies. In the simplest case, this is the energy of translational motion, $1/2\ mc^2$, where c is the velocity of the molecule and m is its mass.

The distribution of molecules among the various energy levels is given by specifying the numbers of molecules:

N_1 having energy ε_1
N_2 having energy ε_2
N_3 having energy ε_3

and so on. Distributing the molecules among the groups characterized by definite energy values ε_i, we thereby introduce the quantum-theory concepts of definite quantized energy values (energy levels) of the molecule. In this treatment, however, the intervals between adjacent levels are not limited in any way and may be as small as desired unless we introduce quantum conceptions. This method of treatment is therefore suitable equally well for both classical and quantum interpretations.

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* In statistics, this quantity is often labelled E.

The total energy of the system will be given by the sum

$$U \equiv E = N_1\varepsilon_1 + N_2\varepsilon_2 + N_3\varepsilon_3 + \ldots = \sum_i N_i\varepsilon_i = \text{const} \qquad (6.34)$$

which is constant by the condition specified. The total number of molecules is also constant:

$$N = N_1 + N_2 + N_3 + \ldots = \sum_i N_i = \text{const} \qquad (6.35)$$

(but the individual numbers N_i may undergo change).

In order to obtain the form of the distribution law most suitable for our task, we take into account some additional characteristics of the energy levels of molecules that follow from experimental (spectral) data and also from quantum theory. The point is that the state of a molecule having a certain energy can also be characterized by other features or properties, which manifest themselves, for example, under the influence of a magnetic field (the Zeeman effect) or an electric field (the Stark effect). In other words, the same (or almost the same) energy value for a molecule can be attained in different ways, i.e., in terms of quantum mechanics, to one and the same energy of a molecule there may correspond several (g_i) eigenstates.

In connection with what has been expounded above, we shall speak of the possibility of existence in a molecule of several energy levels of equal (or nearly equal) energy. Such *multiple* levels are called *degenerate levels* and the degree of degeneracy g_i is also termed the *statistical weight* of the level or its *a priori probability*. The last two terms are evidently associated with the fact that the degeneracy increases the total number of levels of given energy and, accordingly, increases the probability of appearance of molecules of given energy.

Confining ourselves to the classical version of statistics, we shall assume that the state of a system (the macrostate) is uniquely determined by the distribution of distinguishable molecules among the various energy levels, i.e., by specifying the numbers $N_1, N_2, N_3, \ldots$ of molecules having the energies $\varepsilon_1, \varepsilon_2, \varepsilon_3 \ldots$.

To calculate the thermodynamic probability of a state, i.e., the number of ways it is realized, we shall first write the number of ways of distributing N molecules among i groups, i.e., energy states. This number is given by relation (6.27), i.e.,

$$\frac{N!}{N_1!N_2!N_3!\cdots N_j!}$$

However, within each group characterized by a definite energy N_j distinguishable molecules may arrange themselves, without any restrictions in classical statistics, in g_i levels. One molecule can be disposed in g_i levels by g_i ways, two molecules by g_i^2 ways, etc. Hence, for N_i molecules the number of ways for their distribution among the levels will be equal to $g_i^{N_i}$.

The total number of microstates, i.e., the thermodynamic probability of a given macrostate, will now be obtained by multiplying the number of distributions among the groups which has been found above by the numbers of distributions within the groups:

$$W \equiv G = N!\,\frac{g_1^{N_1}}{N_1!}\cdot\frac{g_2^{N_2}}{N_2!}\cdots\frac{g_j^{N_j}}{N_j!} = N!\prod\frac{g_i^{N_i}}{N_i!} \tag{6.36}$$

To the equilibrium state of an isolated system there corresponds a maximum of entropy S from the thermodynamic standpoint and a maximum of the thermodynamic probability W from the statistical viewpoint. The relationship between S and W was derived in Sec. 6.7; it is given by the Boltzmann formula

$$S = \mathrm{k} \ln W$$

or

$$\frac{S}{\mathrm{k}} = \ln W \tag{6.37}$$

Substituting W from Eq. (6.36), we get:

$$\frac{S}{\mathrm{k}} = \ln N! + \sum_i (N_i \ln g_i - \ln N_i!) \tag{6.38}$$

The numbers N and N_i are usually considered to be very large and therefore Stirling's formula, which is the more exact the greater is N, can be applied to the factorials:

$$N! = (2\pi N)^{1/2}\left(\frac{N}{e}\right)^N$$

or

$$\ln N! = \frac{1}{2}\ln(2\pi N) + N\ln N - N$$

The latter relation may be simplified for large N without appreciable error by eliminating the first term on the right-hand side of the equation:

$$\ln N! = N\ln N - N \tag{6.39}$$

The entropy expression (6.38) can now be written as:

$$\frac{S}{\mathrm{k}} = N\ln N - N + \sum_i (N_i \ln g_i - N_i \ln N_i + N_i) =$$

$$= N\ln N + \sum_i (N_i \ln g_i - N_i \ln N_i) \tag{6.40}$$

As we know, at equilibrium W and S have maximum values. In the problem under consideration the equilibrium condition will be such that with all allowable changes in the numbers N_i the sum of the corresponding changes in entropy equals zero:

$$\sum dS_i = \delta S = 0$$

that is, the entropy does not change, remaining at a maximum. We now seek to find the partial entropy changes:

$$dS_1 = \frac{\partial S}{\partial N_1} dN_1 = -\mathrm{k}\left(\ln \frac{N_1}{g_1} + 1\right) dN_1$$

$$dS_2 = \frac{\partial S}{\partial N_2} dN_2 = -\mathrm{k}\left(\ln \frac{N_2}{g_2} + 1\right) dN_2$$

and so on. Summing up all the partial entropy changes, we obtain its total change:

$$\delta S = \sum dS = -\sum_i k\left(\ln \frac{N_i}{g_i} + 1\right) dN_i = 0 \tag{6.41}$$

Hence, the equilibrium condition for the molecular system of interest is the equality

$$\sum_i \left(\ln \frac{N_i}{g_i} + 1\right) dN_i = 0 \tag{6.42}$$

The variables N_i are not all independent since the numbers of molecules are interrelated by the conditions (6.34) and (6.35), which can be written in the form

$$\begin{aligned} \delta N &= \sum dN_i = 0 \\ \delta U &= \sum \varepsilon_i \, dN_i = 0 \end{aligned} \tag{6.43}$$

Using the last two equations, one can easily express two of the quantities dN_i as functions of all the remaining ones. Therefore, all variations in N_i, except for two, may be considered to be mutually independent. To eliminate the dependent variations we make use of the method of undetermined multipliers discovered by Lagrange. In this method, Eqs. (6.43) for δN and δU are multiplied by λ and μ, respectively, and combined with Eq. (6.42):

$$\sum_i \left(\ln \frac{N_i}{g_i} + 1 + \lambda + \mu\varepsilon_i\right) dN_i = 0 \tag{6.44}$$

The arbitrary multipliers λ and μ can be chosen so that two of the coefficients at dN_i in expression (6.44) vanish. Let, for example,

$$\ln \frac{N_1}{g_1} + 1 + \lambda + \mu\varepsilon_1 = 0 \quad \text{and} \quad \ln \frac{N_2}{g_2} + 1 + \lambda + \mu\varepsilon_2 = 0$$

The sum of (6.44) will then retain only those terms which contain the independent variations of the numbers of molecules, dN_i, and the general equality (6.44) can be satisfied only if each of the remaining $i - 2$ coefficients is equal to zero.

Thus, in general, the following equality holds for an equilibrium isolated system consisting of N weakly interacting molecules:

$$\ln \frac{N_i}{g_i} + 1 + \lambda + \mu\varepsilon_i = 0 \tag{6.45}$$

Or, taking antilogs, we have:

$$N_i = \frac{g_i}{e^{(1+\lambda)} e^{\mu\varepsilon_i}} = \frac{g_i}{Be^{\mu\varepsilon_i}} \tag{6.46}$$

or

$$N_i = \frac{1}{B} g_i e^{-\mu\varepsilon_i}$$

where $B = e^{(1+\lambda)}$. Expression (6.46) is the law of distribution of molecules among the various energy levels (written in a general form) in Maxwell-Boltzmann classical statistics.*

Let us find the values of the coefficients B and μ. To do this, we first add up all the numbers of molecules given by relation (6.46):

$$N = \sum_i N_i = \frac{1}{B} \sum_i g_i e^{-\mu\varepsilon_i}$$

whence

$$\frac{1}{B} = \frac{N}{\sum\limits_i g_i e^{-\mu\varepsilon_i}}$$

and the distribution law will assume the form

$$N_i = N \frac{g_i e^{-\mu\varepsilon_i}}{\sum\limits_i g_i e^{-\mu\varepsilon_i}} \tag{6.47}$$

It now remains to find the value of μ which would satisfy the properties of the molecular system. To this end, we take logarithms of expression (6.47):

$$\ln N_i = \ln N + \ln g_i - \mu\varepsilon_i - \ln \left(\sum g_i e^{-\mu\varepsilon_i}\right) \tag{6.48}$$

We then multiply Eq. (6.48) by the number of molecules, N_i, and sum up all similar expressions:

$$\sum N_i \ln N_i = \sum N_i \ln N + \sum N_i \ln g_i - \\ - \sum \mu N_i \varepsilon_i - \sum N_i \ln \left(\sum g_i e^{-\mu\varepsilon_i}\right)$$

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* See also Section 6.9.

Taking cognizance of relations (6.34), (6.35) and (6.40), we can write the last equation in the form:

$$N \ln N + \sum (N_i \ln g_i - N_i \ln N_i) = \mu U + N \ln \left(\sum g_i e^{-\mu \varepsilon_i} \right) = \frac{S}{\mathrm{k}} \tag{6.49}$$

or

$$\frac{S}{\mathrm{k}} = \mu U + N \ln \left(\sum g_i e^{-\mu \varepsilon_i} \right) \tag{6.50}$$

where U is the total energy; S is the entropy of the system of N molecules under consideration. If we now differentiate Eq. (6.50) with respect to the entropy at constant volume, then, assuming the last term to be independent of S, we obtain:

$$\frac{1}{\mathrm{k}} = \mu \left(\frac{\partial U}{\partial S} \right)_v \tag{6.51}$$

But U, the total (internal) energy of the system, is a characteristic function of the variables entropy and volume, i.e., S and v, its total differential is $dU = T\,dS - p\,dv$ and, therefore, as is known,

$$\left(\frac{\partial U}{\partial S} \right)_v = T \tag{6.52}$$

Hence, comparing Eqs. (6.51) and (6.52), we obtain:

$$\mu = \frac{1}{\mathrm{k}T} \tag{6.53}$$

where k is Boltzmann's constant. Thus, Eq. (6.46) can now be written in the form:

$$N_i = \frac{1}{B} g_i e^{-\varepsilon_i/\mathrm{k}T} \tag{6.54}$$

This formula is what is known as the Boltzmann distribution law, which states: *for a molecular system at equilibrium the number of molecules of energy* ε_i *is proportional to the Boltzmann factor* $e^{-\varepsilon_i/\mathrm{k}T}$.

The exponential Boltzmann law is one of the important generalizations in physics and finds numerous applications in its various branches. It plays a significant role in statistical thermodynamics and also in the theory of chemical kinetics. The pre-exponential factor in the Boltzmann equation, $1/B$, depends, as will be shown in the subsequent discussion, on temperature and also on the number and nature of molecules that make up the system. If the inference is repeated for a system consisting, say, of N_{I} molecules of substance I and N_{II} of substance II, we obtain two exponential expressions:

$$N_i = \frac{1}{B_{\mathrm{I}}} g_i e^{-\varepsilon_i/\mathrm{k}T} \tag{6.55}$$

and

$$N_j = \frac{1}{B_{\text{II}}} g_j e^{-\varepsilon_j/kT} \qquad (6.56)$$

from which it follows that if $1/B$ is determined by the properties of the substance, then k is the universal constant.

6.9. Thermodynamic Probability and Distribution Laws in Quantum Statistics

The Maxwell-Boltzmann statistics is based, as is known, on the application of the laws of classical mechanics and on the concept of distinguishability of particles that constitute a system. However, as experimental data were accumulated it became clear that this statistics is approximate; it was also found that it cannot be applied at all to some systems—in the first place to a photon gas and an electron gas in metals. Furthermore, the development of quantum theory has demonstrated that all particles that exist in nature, both elementary and complex molecular particles, should be divided into two classes. The first class of particles is characterized by half-integral spins; such particles are called *fermions*. Examples are electrons, protons and neutrons. The second class of particles is characterized by zero or integral spin; such particles are called *bosons*. Examples are photons and π-mesons. A set of elementary particles forming complex nuclei, atoms and molecules, is a boson or fermion, depending on whether the number of fermions is odd or even. For instance, the deuterium nucleus $(p + n)$ is a boson, the hydrogen atom $(p + e)$ is a boson, but the deuterium $(d + e)$ is a fermion. The nuclei and atoms of helium isotopes also belong to different classes: the ^{3}He nucleus $(2p + n)$ and the ^{3}He atom $(2p + n + 2e)$ are fermions, and the nucleus and atom of ^{4}He are bosons. We shall return to this question at a later time. According to quantum-mechanical data, a boson system is described by *symmetric wave functions**, and for a fermion system the wave function must be *antisymmetric*. In some cases, this gives rise to a significant difference in the behaviour of boson or fermion systems and, in the first place, is reflected in the number of possible microstates in the form of the law of distribution of particles by energy values. Strictly speaking, boson and fermion systems obey different kinds of quantum statistics and do not obey classical statistics. There exist two kinds of quantum statistics: Bose-Einstein statistics and Fermi-Dirac statistics. Let us consider the statistics which was originally developed for light quanta by the Indian scientist Bose and extended by Einstein to molecular systems (bosons).

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* For a more detailed treatment of symmetric wave functions, the reader is referred to the specialized literature.

A system consists of N indistinguishable particles which are distributed among quantum groups or levels. Within each group the energy of particles, ε_i, is the same or almost the same. We shall assume the following distribution of particles among the groups:

N_1 resides in the first group of energy ε_1
N_2 resides in the second group of energy ε_2
. . . .
N_i resides in the ith group of energy ε_i

The total number of particles in the system and the energy of the system as a whole are assumed to be constant:

$$\sum_i N_i = N = \text{const} \quad \text{and} \quad \sum_i \varepsilon_i N_i = E = \text{const} \tag{6.57}$$

The quantum groups or energy levels are degenerate—each group has g_i sublevels with the same energy. In accordance with the properties of symmetric wave functions the bosons that are in a given level can be distributed in any way among the sublevels. In other words, there are no constraints on the number of particles belonging to the given sublevel. Let us first determine the number of ways of distributing N_i indistinguishable particles in the ε_i level among the g_i sublevels. Imagine a box divided by $g_i - 1$ partitions (the vertical lines in the scheme below) into g_i cells. The N_i elements (×) that are in the ε_i level are distributed among the g_i cells of the box. We can write the following scheme:

$$| \times\times\times | \times\times\times\times | \times\times | \times\times\times\times\times | \times\times\times | \times\times |$$

The extreme lines are the boundaries (walls) of the box; they are not involved in permutations. The crosses represent N_i elements in the group. We write the total number of permutations of $g_i - 1$ inner lines and of N_i particles (crosses):

$$(N_i + g_i - 1)! \tag{6.58}$$

But the particles are indistinguishable and their permutations do not give rise to new states. The inversions of identical partitions do not alter the state either. Therefore, the resulting number of permutations obtained should be divided by the number of permutations of particles and of partitions separately, i.e., by $N_i!$ and $(g_i - 1)!$. Hence, the number of ways of distributing N_i indistinguishable elements among the g_i sublevels will be given by

$$\frac{(N_i - g_i + 1)!}{N_i!\,(g_i - 1)!} \tag{6.59}$$

This is for one group. But there are $N_1, N_2, \ldots, N_i \ldots$ particles in different groups. By virtue of the indistinguishability of particles their specified distribution among the groups can be effected in the only way possible. For each group the number of distributions is written in the same form, i.e., (6.59). Since each way of distributing particles in a given group can be combined with any distribution in the remaining groups, the total number of microstates of the system of N particles will be expressed by the product

$$G = \frac{(N_1+g_1-1)!}{N_1!(g_1-1)!}\cdot\frac{(N_2+g_2-1)!}{N_2!(g_2-1)!}\cdots\frac{(N_j+g_j-1)!}{N_j!(g_j-1)!}\cdots =$$

$$\cdots = \prod_i \frac{(N_i+g_i-1)!}{N_i!(g_i-1)!} \tag{6.60}$$

Further, in the same way as before, by virtue of the principle of equal a priori probabilities of microstates the number G may be treated as a measure of the probability of the distribution under study, i.e., *the macrostate of the system.* Thus, just as in Boltzmann statistics, we assume that the probability of a state is proportional to the number of microstates:

$$W = \text{const}\, G \tag{6.61}$$

or, assuming that const = 1, we arrive at the definition of the thermodynamic probability of the state of a boson system:

$$W = G = \prod_i \frac{(N_i+g_i-1)!}{N_i!(g_i-1)!} \tag{6.62}$$

Next, as before, by way of determining the most probable equilibrium distribution, we look for a maximum of ln W. Taking logarithms of Eq. (6.62), we obtain:

$$\ln W = \sum_i \{\ln(N_i+g_i-1)! - \ln N_i! - \ln(g_i-1)!\} \tag{6.63}$$

We assume that N_i and g_i are sufficiently large, neglect unity and make use of Stirling's formula:

$$\ln W = \sum_i \{(N_i+g_i)\ln(N_i+g_i) -$$

$$- N_i - g_i - N_i \ln N_i + N_i - g_i \ln g_i + g_i\} \tag{6.64}$$

Now, as is generally adopted, we treat N_i approximately as a continuous variable and look for the variation of ln W, differentiating Eq. (6.64) with respect to N_i:

$$\delta \ln W = \sum_i \{1 + \ln(N_i+g_i) - 1 - \ln N_i\}\delta N_i = -\sum \ln\left(\frac{N_i}{N_i+g_i}\right)\delta N_i \tag{6.65}$$

At equilibrium $\delta \ln W = 0$ and

$$\sum_i \left(\ln \frac{N_i}{N_i+g_i}\right)\delta N_i = 0 \tag{6.66}$$

But there are also relations that emerge from the constraint equations:

$$\sum \delta N_i = 0 \text{ and } \sum \varepsilon_i \delta N_i = 0 \tag{6.67}$$

Using the method of Lagrangian multipliers, we multiply the first relation by λ and the second by μ and combine the results obtained with Eq. (6.66):

$$\sum_i \left(\ln \frac{N_i}{N_i + g_i} + \lambda + \mu \varepsilon_i \right) \delta N_i = 0 \tag{6.68}$$

As before, we conclude that with an appropriate choice of the multipliers λ and μ the general equality (6.68) will be satisfied if

$$\ln \frac{N_i}{N_i + g_i} + \lambda + \mu \varepsilon_i = 0 \tag{6.69}$$

or

$$N_i = \frac{g_i}{e^{\lambda + \mu \varepsilon_i} - 1} = \frac{g_i}{B e^{\mu \varepsilon_i} - 1} \tag{6.70}$$

where the notation $B = e^{\lambda}$ is introduced. This is precisely the general form of the law of distribution of particles among the energy levels in Bose-Einstein statistics, i.e., for bosons. Comparison of this law with classical laws reveals their characteristic difference: the presence of (—1) in the denominator of the Bose-Einstein law. At a later time we shall discuss the physical consequences that follow from the presence of (—1) in Eq. (6.70); at this point we shall be concerned with the statistics of fermions developed by Fermi and Dirac.

As before, we consider a system composed of N identical and indistinguishable particles, but this time these particles are fermions. Just as in the preceding discussion, we assume that N = const and E = const (6.57); the particles are distributed in quantum groups of constant energy ε_i, which have g_i-fold degeneracy. However, only antisymmetric states are possible for fermions, and this leads to the Pauli exclusion principle. Within the framework of the problem under consideration this principle means that no more than one particle may reside in a given sublevel of a quantum group. In other words, $N_i \leqslant g_i$ if N_i is the number of particles in a given group and g_i is the number of sublevels of a given group (a quantum group). Using once again lines and crosses, we draw up a scheme for the distribution of fermions:

$$| \times || \times | \times ||| \times ||| \times |$$

Let us now find the number of possible ways of distributing particles within a given group. It will be given by the number of combinations of g_i elements with respect to N_i, i.e.,

$$\frac{g_i}{N_i! \, (g_i - N_i)!} \tag{6.71}$$

Without repeating the previous reasonings, we write directly the thermodynamic probability of the macrostate of a fermion system:

$$W = G = \prod_i \frac{g_i}{N_i!\,(g_i - N_i)!} \qquad (6.72)$$

Next, performing the well-known procedure of finding the extremum of ln W, we obtain the distribution law in Fermi-Dirac statistics:

$$N_i = \frac{g_i}{Be^{\mu\varepsilon_i}+1}$$

It is now appropriate to compare all the three distribution laws:

(1) Bose-Einstein:

$$N_i = \frac{g_i}{Be^{\mu\varepsilon_i}-1} \quad \text{or} \quad \frac{g_i}{N_i} + 1 = Be^{\mu\varepsilon_i}. \qquad (6.73)$$

(2) Fermi-Dirac:

$$N_i = \frac{g_i}{Be^{\mu\varepsilon_i}+1} \quad \text{or} \quad \frac{g_i}{N_i} - 1 = Be^{\mu\varepsilon_i} \qquad (6.74)$$

(3) the Maxwell-Boltzmann classical law:

$$N_i = \frac{g_i}{Be^{\mu\varepsilon_i}} \quad \text{or} \quad \frac{g_i}{N_i} = Be^{\mu\varepsilon_i} \qquad (6.75)$$

If the ratio g_i/N_i is large as compared with unity, it may then be neglected in quantum laws. This becomes possible practically for all molecular bosons and fermions at sufficiently high temperatures, i.e., for the following systems:

$$\frac{g_i}{N_i} + 1 \approx \frac{g_i}{N_i} - 1 \approx \frac{g_i}{N_i}$$

and then all the three kinds of statistics yield the same results.

An important conclusion follows from this: *molecular systems* of interest to the chemist (with the exception of ^{4}He at very low temperatures) *are described with sufficient accuracy by classical statistics* (in this case one speaks of the pseudo-classical approximation).

Let us note some special features of bosonic and fermionic gases. For example, the appearance of (—1) in the denominator of the distribution law (6.73) means that the internal energy and pressure of an ideal bosonic gas must be less than the U and p of a gas that obeys classical statistics. Further, if at high energy values the term $Be^{\mu\varepsilon_i}$ is large as compared with unity and the occupation number N_i will be the same as in the case of a classical gas, then at small ε_i the role of unity in the denominator of Eq. (6.73) increases. The number of molecules in the lower energy levels will be greater for a

Bose-Einstein gas than the corresponding number for a gas obeying classical statistics. In other words, a bosonic gas has a tendency to accumulate in the lower energy levels. This is especially pronounced at low temperatures and high densities. Here a process analogous to condensation is possible, which is, however, caused not by the attractive forces operating between molecules but by quantum factors—the formation of a quantum fluid. It is this circumstance that accounts for the special properties of ^{4}He II, which remains to be fluid up to 0°K provided that the pressure does not exceed 25 atm. The behaviour of this fluid corresponds to the properties of the so-called completely degenerate Bose-Einstein gas. It has been reliably observed only in the case of the isotope ^{4}He; ^{3}He does not exhibit such behaviour since it is a fermion; in other molecular systems it is masked by an intermolecular interaction.

6.10. Evaluation of the Molecular Partition Function

Eliminating the factor $1/B$ from Eq. (6.54), just as was done in Sec. 6.8, we write the Boltzmann law in the form

$$N_i = N\frac{g_i e^{-\varepsilon_i/kT}}{\sum_i g_i e^{-\varepsilon_i/kT}}$$

or

$$N_i = N\frac{g_i e^{-\varepsilon_i/kT}}{Q} \tag{6.76}$$

The quantity $Q = \sum g_i e^{-\varepsilon_i/kT}$, which is important for the subsequent discussion, is called the molecular partition function and is the sum of the Boltzmann factors written for all the possible energy states of molecules. In an expansion the partition function for an individual molecule (the molecular partition function) is written as follows:

$$Q = g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + g_3 e^{-\varepsilon_3/kT} + \ldots \tag{6.77}$$

The partition function may also be written in a different form if the lowest-energy state of the molecule is called the *ground* state and the corresponding energy the *zero of energy* ε_0 and the degeneracy of the zero level is designated as g_0:

$$Q = g_0 e^{-\varepsilon_0/kT} + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots = \sum_i g_i e^{-\varepsilon_i/kT} \tag{6.78}$$

where, as has already been said, the summation is over all the possible energy states of the molecule.

In the partition function (6.78) the Boltzmann factors diminish rapidly with increasing ε_i (an exponential function!) and the series expressing Q converge rapidly. Therefore, though, in principle, the summation must be extended to infinity, in practice only a few terms are retained (sometimes, one term is retained).

Let us write the Boltzmann law (6.76) in the form

$$\frac{Q}{N}=\frac{g_i e^{-\varepsilon_i/kT}}{N_i}$$

According to this relation, the partition function is related to the total number of molecules in the same way as the Boltzmann factor taken g_i times is related to N_i, which is the number of molecules oi energy ε_i. Thus, the partition function may be treated as a generalized Boltzmann factor which characterizes the total number of molecules of a given species in the system. From the foregoing it follows that the partition function has no dimensions; it helps one to describe, in a convenient mathematical form, the distribution of energy between the molecules in the system. The numerical value of Q, as will be seen later, depends on the molecular mass, temperature, the volume of the system, i.e., the volume in which the molecules are moving, the internuclear distances and the mode of molecular motion.

6.11. Applications of the Boltzmann Distribution Law to an Ideal Monatomic Gas

In this section we shall be concerned with some applications of the Boltzmann distribution law which usually form the subject matter of the kinetic theory of gases but are in fact a branch of statistical physics. Let us write the Boltzmann law (6.76) in the following form:

$$dN_i=NAg_ie^{-\varepsilon_i/kT} \tag{6.79}$$

This equation differs from the previous one in that the partition function is replaced in it by its inverse quantity, A, and the finite number of molecules N_i with energy ε_i is replaced by an infinitesimal number dN_i because of the actual continuity of the change of the energy of translational motion.

In formula (6.79) g_i is the statistical weight (degeneracy) of a given energy state of a molecule. For a continuously varying energy it is calculated by means of the Heisenberg uncertainty principle, according to which the lowest determinable value of the product of the increments in the coordinate dq and its conjugate momentum dp is given by the condition

$$dq\,dp \gg h \tag{6.80}$$

where h is Planck's constant. Hence, the volume of an elementary cell of the phase space is assumed to be equal to h^f if f is the number of degrees of freedom of motion. We shall first consider one-dimensional motion.

Distribution of Molecules by One Velocity Component. Let the energy of translational motion of a particle in the x direction be $\varepsilon_i = m\dot{x}^2/2$ and the volume of an elementary cell h (one-dimensional motion). Hence, the statistical weight of the given energy state of the molecule with coordinates between x and $x + dx$ and velocities between $\dot{x}$ and $\dot{x} + d\dot{x}$ is written as follows:

$$g_i = \frac{m\, d\dot{x}\, dx}{h} \tag{6.81}$$

Thus, the fraction of molecules that possess the characteristics indicated will be given by the following relation in accordance with Eqs. (6.79) and (6.81):

$$\frac{dN}{N} = A\, \frac{m\, d\dot{x}\, dx}{h}\, e^{-m\dot{x}^2/2kT} \tag{6.82}$$

The proportionality factor A in Eq. (6.82) can be determined by integrating (6.82) over $\dot{x}$ from $-\infty$ to $+\infty$ and over x from 0 to l_x, where l_x is the length of the interval on which the motion is considered. The integration over x directly gives the factor l_x and therefore

$$\frac{dN}{N} = A\, \frac{l_x m}{h}\, e^{-m\dot{x}^2/kT}\, d\dot{x} \tag{6.83}$$

Here the fraction dN/N differs from the previous one, (6.82), though it is written in the same form: this is now the fraction of molecules moving along the interval l_x (which may be one of the dimensions of a rectangular container) with velocities within the range $\dot{x}$ to $\dot{x} + d\dot{x}$. Next, we integrate the fraction given by (6.83) over the velocity:

$$\int \frac{dN}{N} = A\, \frac{l_x m}{h} \int\limits_{-\infty}^{+\infty} e^{-m\dot{x}^2/2kT}\, d\dot{x} = 1 \tag{6.84}$$

The result is equal to unity since the velocities of all the molecules lie within the range from $+\infty$ to $-\infty$.

The determination of the integral in (6.84) is based on the well-known relation

$$\int\limits_{-\infty}^{+\infty} e^{-aq^2}\, dq = (\pi/a)^{1/2}$$

and leads to the expression for A:

$$A = \frac{h}{(2\pi m kT)^{1/2}\, l_x} = \frac{1}{Q_{\mathrm{tr}(1)}} \tag{6.85}$$

where $Q_{\mathrm{tr}(1)}$ is the inverse of A and is called the partition function for one-dimensional translational motion.* Substituting the value of A obtained into Eq. (6.83), we get:

$$\frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-m\dot{x}^2/2kT}\, d\dot{x} \tag{6.86}$$

which is the velocity distribution law for one-dimensional motion. The ratio dN/N in (6.86) may be treated as the probability that the velocity of a randomly chosen molecule in the x direction will be in the range from $\dot{x}$ to $\dot{x} + d\dot{x}$.

Figure 6.3 is a graph of the function (6.86) in the form of the fraction of molecules having velocities within the range $\dot{x}$ to $\dot{x} + 1$.

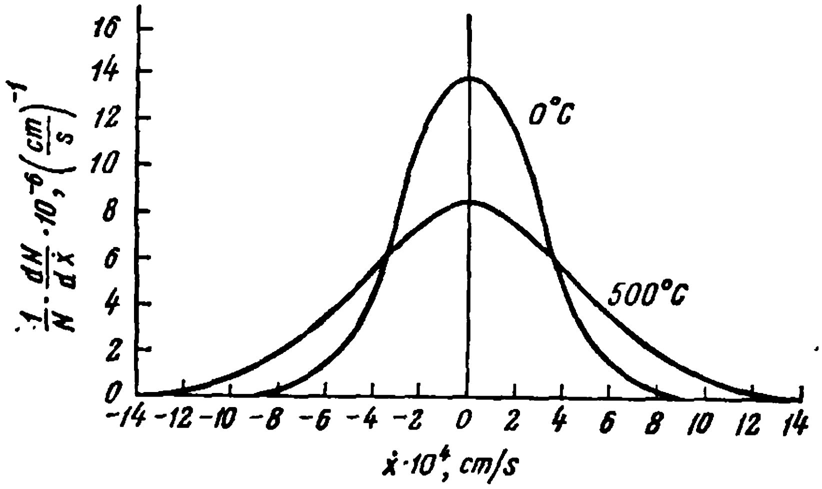

Fig. 6.3. Distribution of molecules by one velocity component for nitrogen at 0 and 500°C (formula 6.86).

The most probable velocity is equal to zero and the fraction of molecules diminishes symmetrically with increasing velocity in the positive and negative directions. This form of velocity distribution appears because one-dimensional motion, i.e., the motion in the direction of a single coordinate axis, is nondegenerate due to the presence of a single direction. In such cases, the probability is given only by an exponential function of the type $e^{-m\dot{x}^2/kT}$ which has the largest value equal to unity at $\dot{x} = 0$.

Using the velocity distribution law (6.86), we find the mean velocity of molecules in a single direction:

$$\bar{\dot{x}} = \frac{\int \dot{x}\, dN}{N} = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty \dot{x} e^{-m\dot{x}^2/2kT}\, d\dot{x} \tag{6.87}$$

---

* The quantity $Q_{\mathrm{tr}(1)}$ is derived in a different way and is considered in more detail in Sec. 6.17.

or

$$\bar{\dot{x}} = \left(\frac{kT}{2\pi m}\right)^{1/2}$$

Here the integration is carried out from 0 to ∞, i.e., all the possible motions in a single positive direction are considered. In other words, the mean absolute value of the velocity x is calculated. From Eq. (6.86) it follows that with both directions, positive and negative, taken into account the mean velocity of one-dimensional motion is equal to zero.

Distribution of Molecular Velocities. The Maxwell Law. If we deal with three-dimensional motion in a volume, then the probability that a molecule will have a velocity within the range $\dot{x}$ to $\dot{x} + d\dot{x}$, $\dot{y}$ to $\dot{y} + d\dot{y}$, and $\dot{z}$ to $\dot{z} + d\dot{z}$ will be given by the product of three equal probabilities of the type of Eq. (6.86), i.e.,

$$\frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT}\, d\dot{x}\, d\dot{y}\, d\dot{z} \qquad (6.88)$$

where $c^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$ is the total velocity of a molecule in a volume. The limits indicated restrict the velocity both in absolute value and in direction; the end of the radius-vector c must lie within the volume $d\dot{x}d\dot{y}d\dot{z}$. We are interested in the distribution of molecules by absolute values of velocity c and not by its directions. Therefore, relation (6.88) must be integrated over all the possible directions. To this end, we pass from Cartesian to spherical coordinates (Figs. 6.4 and 6.5), introducing the following variables: the length of the radius-vector $C = R$, the latitude θ and the longitude Φ. As can be seen from these figures, an element of the phase volume will be expressed with an accuracy of up to infinitesimal values of second order by the relation

$$d\dot{x}\, d\dot{y}\, d\dot{z} = c^2 dc \sin\theta d\theta d\Phi \qquad (6.89)$$

Substituting into (6.88) and integrating over the latitude θ from 0 to π and over the longitude Φ from 0 to 2π, we obtain the fraction of molecules whose velocities are in the range from c to $c + dc$, regardless of the direction in which they may be moving:

$$\frac{dN}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2\, dc \qquad (6.90)$$

This is the Maxwell distribution law for molecular velocities. Figure 6.6 shows three curves of the fraction of molecules having velocities within the range c to $c + 1$ versus c. As can be seen, the curves pass a maximum, which shifts with increasing temperature to higher velocities. As a result, the maximum decreases; this means that as

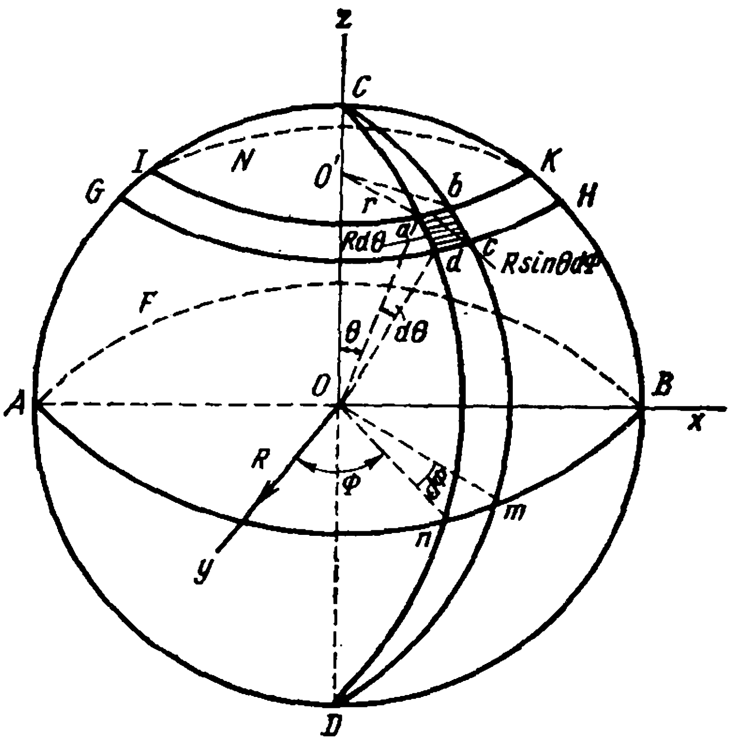

Fig. 6.4. Transformation of Cartesian coordinates to polar (spherical) coordinates:

R—radius of sphere; Φ—longitude counted from the meridian passing through the y axis; θ—latitude counted from the pole C. The two closely spaced meridians and the two parallel latitude circles form an area $abcd$ on the surface of the sphere. The radius of the parallel circle $r = R \sin \theta$ and, hence, the arc $ab = R \sin \theta \, d\Phi$. The arc $ab = R \, d\theta$. The area $abcd$ may be assumed to be a rectangle and hence, it is equal to $R^2 \sin \theta \, d\theta \, d\Phi$ (see Fig. 6.5).

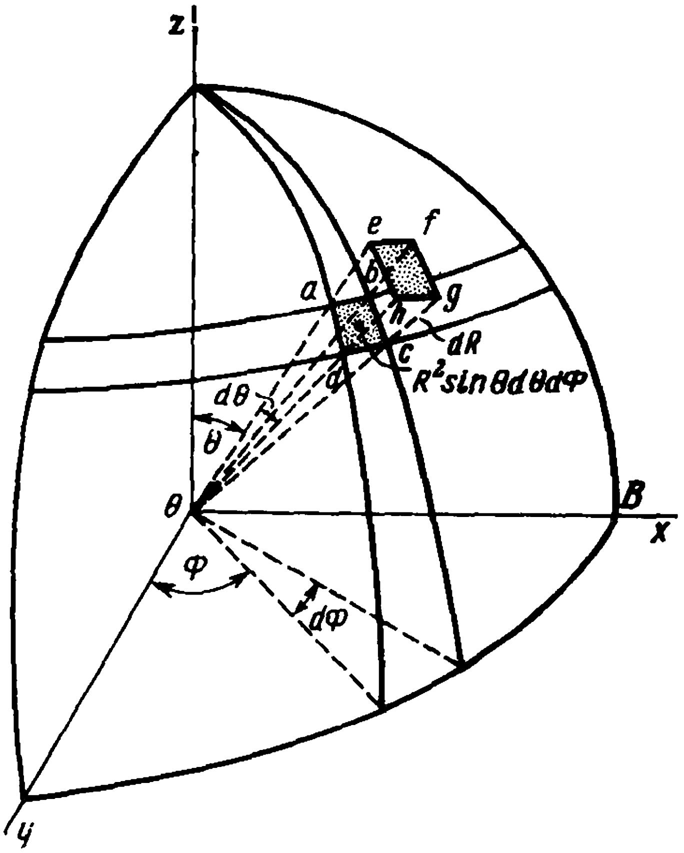

Fig. 6.5. The volume element in polar coordinates:

If the radius of the sphere increases by dR, the area $abcd$ will describe in space a parallelepiped $abcdefgh$, whose volume—a volume element in polar coordinates—is equal to $R^2 \sin \theta \, d\theta \, d\Phi \, dR$. Within infinitesimally small second-order values, it is equal to $dxdydz$, a volume element in Cartesian coordinates.

the temperature is raised the number of molecules having higher velocities increases and the distribution becomes more uniform. The velocity distribution in three dimensions differs significantly from the distribution in one-dimensional motion. Here the maximum lies not at zero velocity but at a certain finite value $c_{\max} = \alpha$, which is called the most probable velocity. According to Eq. (6.90), the probability is given not only by a power function (an exponential), as in one-dimensional motion [formula (6.86)] but also by the pre-exponential factor $4\pi c^2\, dc$. This factor should be regarded as a measure of the statistical weight (degeneracy) of three-dimensional translational motion illustrated in Fig. 6.7 which shows the "velocity space"*. The Maxwell law describes the fraction of molecules, whose velocity vectors lie within the range c to $c + dc$, i.e., if we count from the coordinate origin their ends will be within a spherical layer of radius c and width dc. The volume of the spherical layer, i.e., the portion of the phase space under consideration, may be regarded, in accordance with the Heisenberg uncertainty principle, as being divided into volume elements. The displacement of the end of the vector C inside a volume element does not give rise to new dis-

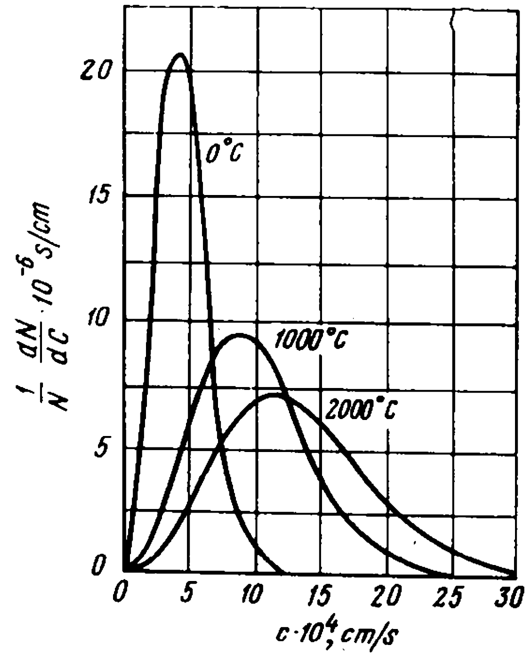

Fig. 6.6. The velocity distribution of nitrogen molecules at various temperatures.

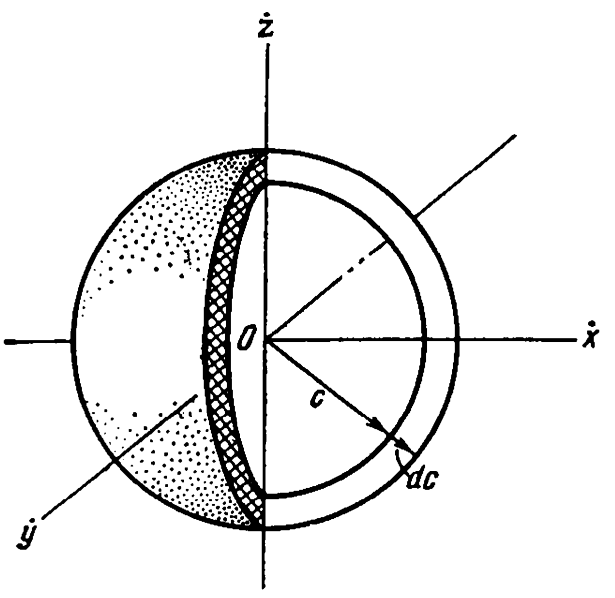

Fig. 6.7. Explaining the significance of the statistical weight (degeneracy) of levels of translational motion.

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* The more appropriate term is the momentum space, but since in this particular case the momenta are simply the quantities of motion $m\dot{x}$, $m\dot{y}$ and $m\dot{z}$, i.e., quantities which are proportional to velocities, the essence of the matter is not changed.

tinguishable velocity directions. Therefore, *the number of distinguishable directions of the vector c is proportional to the number of volume elements in the spherical layer, i.e., to the volume of the spherical layer* $4\pi c^2\, dc$. It is this factor that should be regarded as a measure of the statistical weight (degeneracy) of three-dimensional translational motion.

To the maximum of the function $(1/N)\, dN/dc$ there corresponds, as has already been said, the most probable velocity α. Let us find it by means of an ordinary method. Differentiating $y = (1/N)\,(dN/dc)$ with respect to c and equating the derivative to zero, we obtain:

$$\alpha = \left(\frac{2kT}{m}\right)^{1/2}$$

Thus, the most probable velocity is proportional to the square root of temperature. The mean velocity $\bar{c}$ of molecules at a given temperature differs from α. It is calculated by multiplying dN/N by c and integrating* between zero and infinity:

$$\bar{c} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-mc^2/2kT} c^3\, dc = \left(\frac{8kT}{\pi m}\right)^{1/2} \qquad (6.91)$$

An important role in the kinetic theory of gases is played by the so-called root-mean-square velocity. It can be found by means of a preliminary calculation of the mean square of velocity c^2:

$$\bar{c^2} = \frac{\int c^2\, dN}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty e^{-mc^2/2kT} c^4\, dc \qquad (6.92)$$

Integration** of (6.92) yields

$$\bar{c^2} = \frac{3kT}{m} \qquad (6.93)$$

---

* The integral $\int_0^\infty e^{-aq^2} q\,dq = 1/2a$ is elementary. If we differentiate it with respect to the parameter a, we obtain directly: $\int_0^\infty e^{-aq^2} q^3 dq = 1/2a^2$.

** We proceed from the tabulated integral $\int_{-\infty}^{+\infty} e^{-aq^2} dq = (\pi/a)^{1/2}$. Differentiating it with respect to the parameter a, we get: $\int_{-\infty}^{+\infty} q^2 e^{-aq^2} dq = \frac{\pi^{1/2}}{2a^{3/2}}$.

Extracting the square root, we find the root-mean-square velocity:

$$u = \sqrt{\overline{c^2}} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3}{2}\right)^{1/2} \alpha \approx 1.224\alpha \tag{6.94}$$

Thus, all the velocities found, while being proportional to $(T/m)^{1/2}$, differ in absolute value and are interrelated as follows:

$$u > \bar{c} > \alpha$$

As has already been said, the root-mean-square velocity plays an important part in the kinetic theory of gases since the pressure of a gas and the energy of translational motion of its molecules are given by

$$pv = RT = \frac{1}{3} N_A mu^2 \tag{6.95}$$

and

$$E = \frac{1}{2} N_A mu^2 = \frac{3}{2} RT \tag{6.96}$$

Hence, the molar heat capacity of a monatomic ideal gas, or the part of the heat capacity of a polyatomic gas pertaining to translational motion, is obtained by differentiating Eqs. (6.95) and (6.96) with respect to temperatures:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{3}{2} R \tag{6.97}$$

and

$$C_p = C_v + R = \frac{5}{2} R \tag{6.98}$$

6.12. Negative Temperatures

The concept of the extension of the Kelvin temperature scale to negative values appeared for the first time in 1950. The essence of the problem is as follows. The well-known thermodynamic relation, namely the derivative of the internal energy U with respect to the entropy S

$$\left(\frac{\partial U}{\partial S}\right)_v = T \quad \text{or} \quad \left(\frac{\partial S}{\partial T}\right)_v = \frac{1}{T} \tag{6.99}$$

We differentiate once again with respect to the parameter a: $\int_{-\infty}^{+\infty} q^4 e^{-aq^2} dq = (3/4)\, \pi^{1/2}/a^{5/2}$. Now, from symmetry considerations, we may write directly:

$$\int_0^{-\infty} q^4 e^{-aq^2}\, dq = \frac{3}{8} \frac{\pi^{1/2}}{a^{5/2}}$$

may be treated as the definition of the absolute temperature. The temperature T is positive if the energy of the system increases with increasing entropy. In ordinary systems, say, a gas or a crystalline body, the number of energy levels is infinitely large and as the energy is added an ever increasing number of particles jump to levels with a greater energy—the disorder of the state increases and so does the entropy. The temperature of such a system is positive. To make it negative the increase of energy must be accompanied by a decrease in entropy. Is it conceivable? With an infinite number of energy levels this is impossible. Indeed, if we denote the number of molecules in a level of energy ε_i as N_i and at the zero of energy ε_0 as N_0, then, according to the Boltzmann law (6.76), we can write down the relation

$$\frac{N_i}{N_0} = e^{\frac{\varepsilon_i - \varepsilon_0}{kT}} \qquad (6.100)$$

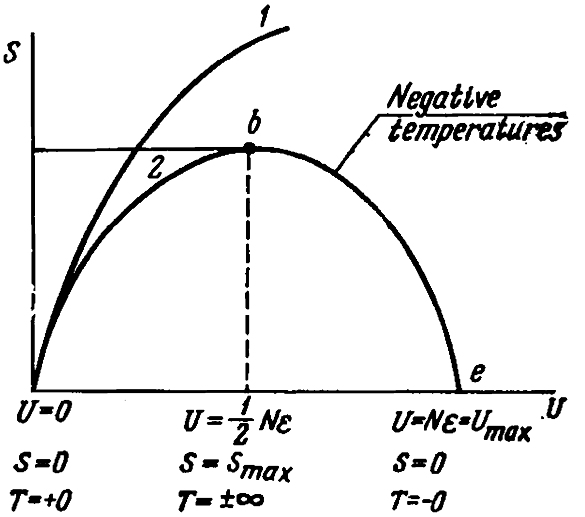

Fig. 6.8. Entropy as a function of energy:

Curve 1—for ordinary systems with an infinite number of levels; curve 2—for systems with a limited number of levels when "negative temperatures" are conceivable.

If the number of levels is infinite, as is the case in ordinary systems, the ratio N_i/N_0 is always less than unity and the temperature is positive ($T > 0$). The situation is different if the number of energy levels in systems is finite. Let us consider the simplest version of this case, assuming the existence of only two levels with energies 0 and ε, between which there are distributed N particles. At low temperatures all the particles are in the ground level and the system has the zero of energy. This is the state of maximum order; its thermodynamic probability equals unity and the entropy is zero. As the energy is supplied to the system (the temperature is raised) an ever increasing number of particles are transferred to the upper level of energy ε. The disorderliness of the state increases and so does the entropy. According to the Boltzmann law in the form $N_\varepsilon/N_0 = e^{-\varepsilon/kT}$, the ratio of the numbers of molecules in the two levels is equal to unity only at $T = \infty$. This state corresponds to the maximum disorder of the system of interest with two energy levels and to the entropy maximum (Fig. 6.8). The energy of the system at this point is $U = 1/2\, N\varepsilon$. In principle, we may imagine the *inversion* of the levels, i.e., the situation where the upper energy level is populated to a greater extent than the lower one. This is supposed to be associated with further supply of energy to the system effected this time in some non-thermal way, as a result of which the disorder of the state and, hence, the entropy will be decreased. In the limit, when all the particles are found to be in the upper energy level, the system again reaches the state of maximum order and the entropy turns to zero. The energy in this case attains a limiting value: $U = N\varepsilon$. From a formal standpoint, in agreement with Eq. (6.99), the states of the system with $N_\varepsilon > N_0$ (the portion of the curve *bc* in Fig. 6.8) may be regarded as the negative-temperature domain, which, however, has no analogue in ordinary systems. When the point *b* is passed, the derivative $dS/dU = 1/T$ changes sign and becomes negative. But in this case, as we may assume, the temperature changes discontinuously from $+\infty$ to $-\infty$. Then, as the level inversion is increased it decreases in absolute value, tending to $T = -0$. In other words, a body with a negative temperature must be "hotter" than a body at any positive temperature. It may also be said that in the negative-temperature domain a more heated body has a lower absolute value of temperature. The entire range of variation of temperatures may be represented by the following sequence in increasing order:

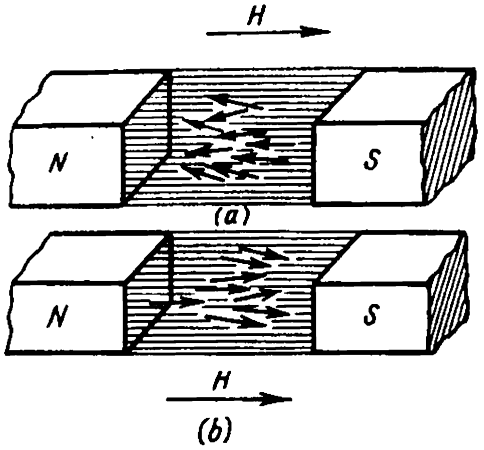

Fig. 6.9. Nuclear moments in a magnetic field as an example of systems with a limited number of energy levels:

a—upper energy level for antiparallel orientation; *b*—lower energy level for parallel orientation.

$$+0^\circ,\ +1^\circ,\ +2^\circ,\ \ldots,\ +\infty,\ -\infty,\ \ldots,\ -2^\circ,\ -1^\circ,\ -0^\circ$$

But to what physically realizable systems could the concepts considered above be applied? As has already been said, they cannot be applied to ordinary systems since there must be an upper bound to the energy. However, in ordinary systems there are sometimes so-called subsystems, which interact weakly with the main system and which have a limited number of energy levels. The weak interaction between a subsystem and the main system is required for the thermal equilibrium between them to be established slowly. And if the thermal equilibrium in the subsystem itself sets in rapidly, then we can speak of its temperature as being different from the temperature of the main system. An example of a subsystem is a set of nuclear spins of lithium ions in a crystal of lithium fluoride. For the sake of simplicity, suppose that we have two possible orientations of the spins in a magnetic field—a parallel spin of lower energy and an antiparallel spin of higher energy (Fig. 6.9). Usually, there are much less spins with antiparallel than those with parallel orientation; the subsystem is in equilibrium with itself and with the crystal lattice as a whole. In this case, the temperature is everywhere positive. However, if (as was the case in experiments carried out by Purcell and Pound) the magnetic field is reversed rapidly, the spins will not be able to follow and the greater part will remain to be oriented antiparallel. Thus, the inversion of the levels occurs, i.e., the upper energy level has a higher population and one can formally speak of the negative temperature of the subsystem of nuclear spins. After the lapse of a certain period of time (5-30 min) the subsystem, while interacting and being brought up to an equilibrium with the main system, is "cooled" and assumes an ordinary positive temperature.

Thus, the negative-temperature concept can be applied formally in special cases where the addition of energy from without creates a pseudo-equilibrium (more exactly, a nonequilibrium) subsystem of inverted levels. The inversion of energy levels can also be effected by the absorption of light, as in lasers, or by microwave radiation, the latter method being used for the operation of masers. Whether it is appropriate to use the term "negative temperature" in all these cases is the question of terminology.

6.13. The Partition Function in Classical and Quantum Statistics

Let us return to the Boltzmann law (6.76). As will be shown later (Sec. 6.14), the partition function may be related with the thermodynamic properties of a system. However, if the thermodynamic functions of an ideal gas were determined from the molecular partition function, we would come to unsatisfactory results. Indeed, while correct results could have been obtained for the internal (total) energy, heat capacity and pressure, the calculated entropy, for example, would have been lower than that obtained on the basis of thermal data by about two entropy units (about 2 cal/deg·mole). Careful examination of the problem shows that there is no sufficient ground for attempting to calculate the entropy and a number of other thermodynamic functions that include the entropy and are, in essence, the properties of the system as a whole from the molecular partition function. In this connection it is necessary to introduce the concept of the partition function of the system.

When considering the state of the system as a whole as a function of the state of its constituent particles (molecules) two cases must be distinguished. In the first case, the properties of the system are believed to be dependent on which individual particles exhibit which characteristics, i.e., in this case the particles are considered to be distinguishable. In the second case, the properties of the system depend only on the number of particles distributed among the groups according to the characteristics displayed by them. The particles themselves are indistinguishable.

Let us first consider the first case.

(a) Distinguishable particles (a Maxwell-Boltzmann system). Let the system consist of identical molecules; each molecule may have an identical number of energy states. The particles are assumed to be distinguishable, so that the state of the system as a whole must be characterized by specifying the state of each of N identical, distinguishable particles. In accordance with the terminology adopted, this kind of system is called a Maxwell-Boltzmann system.

If the states of N individual particles are labeled as the subscripts $i_1, i_2, \ldots, i_N$, then in the absence of the interaction between them the energy of the system will be given by the relation

$$E_{i_1, i_2, \ldots, i_N} = \varepsilon_{i_1} + \varepsilon_{i_2} + \ldots + \varepsilon_{i_s} + \ldots + \varepsilon_{i_N}$$

Each of the specified values of the subscripts, $i_1, i_2, \ldots, i_s, \ldots$ $\ldots, i_N$, would correspond to an individual state of system as a whole. The partition function of the system will be written as

$$Z = \sum e^{-(\varepsilon_{i_1} + \varepsilon_{i_2} + \ldots + \varepsilon_{i_N})/kT} \tag{6.101}$$

where the summation is carried out over all the possible values of $i_1, i_2, \ldots, i_N$.

The expression for Z can be simplified by factorizing into the product of factors of the type $e^{-\varepsilon_i/kT}$ since the set of energy states is the same for all the molecules. Thus,

$$Z = (\sum_i e^{-\varepsilon_i/kT})^N = Q^N \tag{6.102}$$

where ε_i are the energy states of a single molecule; Q is the molecular partition function. In writing relation (6.102) we imply the summation over i separate levels. If the degeneracy is taken into account (when several levels have the same energy), the formula obtained may be rewritten in the form

$$Z = (\sum_i g_i e^{-\varepsilon_i/kT})^N \tag{6.103}$$

where g_i is, as before, the number of distinguishable levels of equal energy.

Thus, we have derived an expression for the partition function of a Maxwell-Boltzmann system consisting of N distinguishable noninteracting particles.

We shall now turn to the consideration of the second case.

(b) Indistinguishable particles. Bose-Einstein and Fermi-Dirac gases. Consider a system (a gas) whose state is defined simply by specifying the number of particles, which are in various possible states. In contrast to Maxwell-Boltzmann statistics, here it is immaterial which particles are in which states. In other words, the particles are considered to be indistinguishable. It should be noted at this point that this method of treatment points to the possibility of existence of special, so-called *degenerate* states of the system. Here the term "degenerate" is used in a different sense than in the preceding section and refers to the system as a whole. This type of degeneracy manifests itself at low temperatures and high pressures and it does so the more readily the smaller the mass of the particles: for one thing, the outcome is that upon approach to absolute zero the entropy of liquid ^{4}He becomes equal to zero. The discussion of this type of degeneracy is beyond the scope of our treatment since we may confine ourselves to sufficiently rarefied gases, which are at not too low temperatures.

Generally, in statistics the terms "degeneracy" and "degenerate" are used in three different senses. First, the degeneracy is the number of levels having the same energy, i.e., the statistical weight of energy levels, or the multiplicity (in application to electronic states).

Second, we speak of the quantum degeneracy of the system, when classical statistics becomes invalid and it is necessary to resort to quantum statistics. This type of degeneracy in molecular systems practically reveals itself only at low temperatures in the helium isotope ^{4}He, and for other gases it is masked by an intermolecular interaction, this kind of interaction being weak in helium.

Third, there is the degeneracy of the various kinds of motion. For example, at moderate temperatures no vibrational motion of diatomic molecules is excited, i.e., it is degenerate. As a result, the heat capacity $C_v = 5/2R$. It is summed up of 5 $(1/2R)$, in accordance with the principle of equal distribution: $1/2R$ per each of three translational degrees of freedom and each of two vibrational degrees of freedom. Vibrational motion at moderate temperatures does not make a contribution to the heat capacity—it is degenerate (see Fig. 6.14).

So, let us consider a sufficiently rarefied gas consisting of N noninteracting particles, each of which may be in state with energies ε_k, ε_e, ε_m, . . ., these states being common to all the particles.

Using the symbols ε_1, ε_2, . . ., ε_N for the possible values of energy of N molecules forming the system, we write the energy of the system as the sum:

$$E = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N \tag{6.104}$$

The total number of terms on the right-hand side is equal to N. Designating the number of molecules which are in identical energy states by N_k, N_e, N_m . . . [these represent the numbers of recurring terms in the sum (6.104)], we find that the reduced value of E can be obtained by

$$\frac{N!}{N_k!N_e!N_m! \ldots}$$

ways simply through permutations of the indices 1 . . . N for the energies ε_i. In the preceding section, while dealing with a system consisting of distinguishable particles, we assumed that such permutations lead to different states of the system as a whole. In this case, however, since the particles are assumed to be indistinguishable, this expression implies only the number of identical states. Proceeding from what has been said, we can write the partition function for a system (an ideal gas) composed of N identical indistinguishable elements:

$$Z=\sum_{\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_N}\frac{N_k!N_e!N_m!\ldots}{N!}e^{-\frac{\varepsilon_1+\varepsilon_2+\ldots+\varepsilon_N}{kT}} \tag{6.105}$$

where the pre-exponential factor excludes the possibility of taking into account identical states in the partition function more than once.

Further, considering the use of expression (6.105), two cases may be distinguished. In the first, summation is carried out over all the possible values of $\varepsilon_1, \ldots, \varepsilon_N$. This method is employed in Bose-Einstein statistics originally developed by Bose for light quanta and applied by Einstein to gas molecules. In the second case, Pauli's exclusion principle is used, according to which the terms in which two or more energy values $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N$ refer to the same state are eliminated. In such cases we speak of Fermi-Dirac statistics developed for an electron gas.

We now simplify expression (6.105), applying it to a gas which is at a sufficiently high temperature and which occupies a large volume. Since there are a very large number of energy states, we may assume that there is no more than one molecule per each state. This allows us to set all the factorials $N_k!\ N_e!\ N_m!\ \ldots$ equal to unity. Thus, for any gas we obtain the following partition function as a satisfactory approximation:

$$Z=\frac{1}{N!}\sum_{1,\varepsilon_2,\ldots,\varepsilon_N}e^{-\frac{\varepsilon_1+\varepsilon_2+\ldots+\varepsilon_N}{kT}} \tag{6.106}$$

which takes account of all the possible values of ε for the energies of N particles. The expression summed can, however, be factorized into the product of factors of the type $\exp(\varepsilon_k/kT)$ and rewritten as follows:

$$Z=\frac{1}{N!}\left(\sum_k e^{-\varepsilon_k/kT}\right)^N \tag{6.107}$$

In this new expression the summation is carried out over all the energy states of one molecule of the type considered. We can also take into account the degeneracy of energy levels; then, the partition function of an ideal gas consisting of N identical molecules is written in the form

$$Z=\frac{1}{N!}\left(\sum_i g_i e^{-\varepsilon_i/kT}\right)^N=\frac{1}{N!}Q^N \qquad (6.108)$$

Now the summation has been carried out over all the energy levels and not over each individual state. Comparing expression (6.108) with the expression derived earlier, (6.103), we see that the condition for the indistinguishability of particles leads to the appearance in the partition function of the system of an additional factor, $1/N!$.

If we take the logarithm of Z in Eq. (6.108), we obtain:

$$\ln Z = N\ln Q - \ln N!$$

or, using Stirling's formula, $\ln N! = N\ \ln N - N + \frac{1}{2}\ln 2\pi N$,

$$\ln Z = N\ln Q - N\ln N + N - \frac{1}{2}\ln 2\pi N =$$

$$= N\left(\ln Q - \ln N + 1 - \frac{1}{2N}\ln 2\pi N\right)$$

The last term in parentheses tends to zero with increasing N and we neglect it, assuming N to be very large; then,

$$\ln Z = N\ln\frac{Qe}{N} \qquad (6.109)$$

The partition function of the system is also called the *grand partition function.*

6.14. Partition Function, Thermodynamic Functions and the Equilibrium Constant

The Total (Internal) Energy and Enthalpy. In order to calculate the total (internal) energy of a system, we differentiate the grand partition function (6.108) with respect to temperature at constant volume:

$$\left(\frac{\partial Z}{\partial T}\right)_v=\frac{N}{N!}Q^{N-1}\left(\frac{\partial Q}{\partial T}\right)_v=\frac{N}{N!}Q^{N-1}\left(\frac{g_1\varepsilon_1}{kT^2}e^{-\frac{\varepsilon_1}{kT}}+\right.$$

$$\left.+\frac{g_2\varepsilon_2}{kT^2}e^{-\frac{\varepsilon_2}{kT}}+\ldots\right)$$

Multiplying the derivative by kT^2 and dividing by Z, we get:

$$kT^2\frac{\partial\ln Z}{\partial T}=kT^2N\frac{\partial\ln Q}{\partial T}=$$

$$=\left(\frac{g_1\varepsilon_1}{Q}e^{-\frac{\varepsilon_1}{kT}}+\frac{g_2\varepsilon_2}{Q}e^{-\frac{\varepsilon_2}{kT}}+\ldots+\frac{g_i\varepsilon_i}{Q}e^{-\frac{\varepsilon_i}{kT}}+\ldots\right)$$

Since, according to Eq. (6.76), $g_i e^{-\varepsilon_i/\mathrm{k}T}/Q = N_i/N$, we have for one mole of gas:

$$U = \mathrm{k}T^2 \frac{\partial \ln Z}{\partial T} = RT^2 \frac{\partial \ln Q}{\partial T} = \varepsilon_1 N_1 + \varepsilon_2 N_2 + \ldots$$

$$\ldots + \varepsilon_i N_i = \sum \varepsilon_i N_i$$

Here it should be kept in mind that we calculate not the absolute value of the total (internal) energy, as might seem to be the case, but the excess of energy over a certain zero level U_0 (or E_0), which is most conveniently assumed to be the energy at absolute zero. The energy values for a molecule, as given by the expansion (6.34), should have been written in the form: $\varepsilon_1 + \varepsilon_0$, $\varepsilon_2 + \varepsilon_0$, $\varepsilon_3 + \varepsilon_0 \ldots$, where ε_0 is the indeterminable value of the zero of energy of the molecule. If what has been said is taken into account, the expression for the internal energy should be written as:

$$U - U_0 = E \quad E_0 = \mathrm{k}T\left(\frac{\partial \ln Z}{\partial T}\right)_v = RT^2\left(\frac{\partial \ln Q}{\partial T}\right)_v \tag{6.110}$$

Note that the use of the grand and molecular partition functions gives, in this case, similar formulas; the only difference is in the factors k and R. In calculating the individual partition functions (Sec. 6.17) it will be shown that Q incorporates, as a cofactor, the quantity RT/p. We may therefore write:

$$Q = q'\frac{RT}{p} = q'v \quad \text{and} \quad \ln Q = \ln q' + \ln \frac{RT}{p}$$

As seen from this equation, the derivatives ln Q with respect to temperature at v = const and p = const have different values. For example, if

$$\left(\frac{\partial \ln Q}{\partial T}\right)_v = \left(\frac{\partial \ln q'}{\partial T}\right)_v$$

then

$$\left(\frac{\partial \ln Q}{\partial T}\right)_p = \left(\frac{\partial \ln q'}{\partial T}\right)_p + \frac{1}{T}$$

But q' is independent of the volume or pressure, and its derivatives in both expressions are equal. Therefore, if

$$U - U_0 = RT^2\left(\frac{\partial \ln Q}{\partial T}\right)_v = RT^2 \frac{d \ln q'}{\partial T}$$

then, using the derivative at constant pressure, we obtain:

$$RT^2\left(\frac{\partial \ln Q}{\partial T}\right)_p = RT^2 \frac{d \ln q'}{\partial T} + RT$$

But the first term on the right-hand side of the last equation is equal to $U - U_0$ and the second term to $RT = pv$; therefore, on the basis of the preceding expression we obtain the enthalpy of one molecule of an ideal gas:

$$H - H_0 = U - U_0 + pv = U - U_0 + RT = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_p \qquad (6.111)$$

since $H_0 = U_0$ at $T = 0$.

Heat Capacity at Constant Volume. The heat capacity at constant volume is determined by means of the well-known thermodynamic relation:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad (6.112)$$

Hence, differentiating relation (6.112) with respect to temperature, we find that

$$C_v = \mathrm{k}\left[2T\left(\frac{\partial \ln Z}{\partial T}\right)_v + T^2\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_v\right] = \\ = R\left[2T\left(\frac{\partial \ln Q}{\partial T}\right)_v + T^2\left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_v\right] \qquad (6.113)$$

In this case too the use of Z and Q leads to identical results.

Entropy. As we know, the change in entropy of the system, which undergoes change in an equilibrium process, is equal to the reduced heat:

$$dS = \frac{\delta Q}{T} \qquad (6.114)$$

At constant volume $\delta Q = C_v\, dT$ and, in view of relation (6.113), we have

$$S - S_0 = \int_0^T \frac{C_v}{T}\, dT = \mathrm{k}\int_0^T \left[2\left(\frac{\partial \ln Z}{\partial T}\right)_v + T\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)\right] dT$$

The first integral is taken directly, and the second is determined by parts:

$$S - S_0 = \mathrm{k} \ln Z - \mathrm{k} \ln Z_0 + \mathrm{k}T\left(\frac{\partial \ln Z}{\partial T}\right)_v \qquad (6.115)$$

In what follows, by equating S_0 to k ln Z_0, i.e., by introducing the statistical analogue of the Planck's postulate, we can write a relation which establishes the connection between the entropy and the grand partition function:

$$S = \mathrm{k} \ln Z + \mathrm{k}T\left(\frac{\partial \ln Z}{\partial T}\right)_v \qquad (6.116)$$

But if we make use of the molecular partition function Q, then, according to Eq. (6.109), the expression for S will assume a somewhat different form:

$$S = R \ln \frac{Qe}{N_A} + RT\left(\frac{\partial \ln Q}{\partial T}\right)_v \tag{6.117}$$

where N_A is Avogadro's number.

As can be seen, formulas (6.116) and (6.117) are not identical since they differ not only in the factors outside the logarithm but also in the logarithmic function itself.

It is essential to note that formulas (6.116) and (6.117), unlike formulas (6.110) and (6.111), give not the difference but the absolute value of the thermodynamic function—the entropy.

The Helmholtz Free Energy. By definition, the Helmholtz free energy is $F = U - TS$. Substituting the expressions for the internal energy, (6.110), and the entropy, (6.116), we obtain:

$$F - U_0 = -\mathrm{k}T \ln Z = -RT \ln \frac{Qe}{N_A} \tag{6.118}$$

The Gibbs Free Energy. By definition, the Gibbs free energy is given by

$$G = F + pv = U - TS + pv$$

or, for one mole of an ideal gas, using Eq. (6.118), we find that

$$G - H_0 = F - U_0 + RT = -\mathrm{k}T \ln Z + RT = -RT \ln \frac{Q}{N_A} \tag{6.119}$$

It should be emphasized once again that in all the formulas containing the gas constant R, say, (6.117), (6.118) and (6.119), the calculation is carried out per 1 mole and also that at absolute zero the values of the thermodynamic potentials are equal, i.e.,

$$U_0 = H_0 = F_0 = G_0$$

The Chemical Potential and the Equilibrium Constant. Before we derive a statistical expression for the equilibrium constant of a chemical reaction, let us consider an ideal gas mixture which is composed of N_1 molecules of the first component, N_2 molecules of the second component, and so on. Since a collection of particles of each of the components may be treated as an independently coexisting system, a subsystem, the grand partition function of the mixture should be written in the form of the product of the corresponding partition functions for the subsystems:

$$Z_{\text{mixture}} = Z_1 Z_2 Z_3 \ldots$$

or

$$\ln Z_{\text{mixture}} = \sum_i \ln Z_i = \sum N_i \ln \frac{Q_i e}{N_i} \tag{6.120}$$

which takes into account relation (6.109) connecting the grand partition function Z and the molecular partition function Q. The Helmholtz free energy of the mixture will be written, in agreement with (6.118), as follows:

$$(F-U_0)_{\text{mixture}}=F_{\text{mixture}}-\sum U_{0i}=-\mathrm{k}T\ln Z_{\text{mixture}}=$$
$$=-\mathrm{k}T\sum N_i\ln\frac{Q_i e}{N_i}$$

where $\sum U_{0i}$ is the sum of the zero energies of the components equal to the zero of energy of the mixture. Next, differentiating F_{mixture} with respect to the number of molecules of a component, we take into consideration that the zero of energy is an additive function and therefore the derivative $\sum U_{0i}$ with respect to N_i will give the zero of energy of the component per molecule, u_{0i}. Thus, the chemical potential of the ith component of the mixture will be given by

$$\bar{\mu}_i\equiv\left(\frac{\partial F_{\text{mixture}}}{\partial N_i}\right)_{T,\,v,\,N_j\neq N_i}=-\mathrm{k}T\ln\frac{Q_i}{N_i}+u_{0i}$$

or, per one mole,

$$\mu_i=N_{\mathrm{A}}\bar{\mu}_i=-RT\ln\frac{Q_i}{N_i}+U_{0i}\qquad(6.121)$$

where U_{0i} is the molar zero energy of the component.

We shall now turn our attention to the chemical potential; we first write the equation of a generalized reaction:

$$\nu_1\mathrm{A}_1+\nu_2\mathrm{A}_2+\ldots\rightleftharpoons\nu_1'\mathrm{A}_1'+\nu_2'\mathrm{A}_2'+\ldots$$

where A_i are the participants in the reaction; ν_i are the numbers of moles.

The general condition for chemical equilibrium is

$$\sum(\nu_i\mu_i)=0\qquad(6.122)$$

where the sum is over to the reactants and products.

Substitution of the expression for the chemical potential, (6.121), into the equilibrium condition (6.122) yields

$$RT\left\{\nu_1'\ln\frac{Q_1'}{N_1'}+\nu_2'\ln\frac{Q_2'}{N_2'}+\ldots-\nu\ln\frac{Q_1}{N_1}-\nu_2\ln\frac{Q_2}{N_2}-\ldots\right\}=$$
$$=\nu_1'U_{01}'+\nu_2'U_{02}'+\ldots-\nu_1U_{01}-\nu_2U_{02}=\ldots=\Delta U_0\qquad(6.123)$$

where ΔU_0, i.e., the algebraic sum of the zero energies of the participants in the reaction, has the physical significance of the heat effect of reaction at absolute zero. This quantity is illustrated in Fig. 6.10 for the simplest reaction A $\rightleftharpoons$ B. Here the energy is counted off from the lowest vibrational level of the molecule A, and the heat of reaction, $\Delta\varepsilon_0$, is equal to the difference between the zero energies of the molecules.

Now it is useful to introduce a new function—the partition function of the component per unit volume:

$$q_i = \frac{Q_i}{v} \tag{6.124}$$

where v is the volume of the system. Using q_i, we rewrite expression (6.123) in the form

$$\ln \frac{q_1'^{\nu_1'} q_2'^{\nu_2'} \ldots \left(\frac{N_1}{v}\right)^{\nu_1} \left(\frac{N_2}{v}\right)^{\nu_2'} \ldots}{q_1^{\nu_1} q_2^{\nu_2} \ldots \left(\frac{N_1'}{v}\right)^{\nu_1'} \left(\frac{N_2'}{v}\right)^{\nu_2'} \ldots} = \frac{\Delta U_0}{RT}$$

Since the ratio $N_i/v = c_i$, i.e., is the concentration of a given component expressed by the number of molecules per unit volume, the last relation is readily transformed to the following:

$$K_c = \frac{c_1'^{\nu_1'} c_2'^{\nu_2'} \ldots}{c_1^{\nu_1} c_2^{\nu_2} \ldots} = \frac{q_1'^{\nu_1'} q_2'^{\nu_2'}}{q_1^{\nu_1} q_2^{\nu_2}} e^{-\frac{\Delta U_0}{RT}} \tag{6.125}$$

Equation (6.125) is the expression of the law of mass action written in the form of the equilibrium constant in terms of the concentration and the partition functions q_i. The equilibrium constant is written here in the same manner as in terms of the concentrations but with the addition of the factor exp $(-\Delta U_0/RT)$, which contains, as has been mentioned, the heat effect of reaction at absolute zero, i.e., $\Delta U_0 \equiv \Delta E_0$.

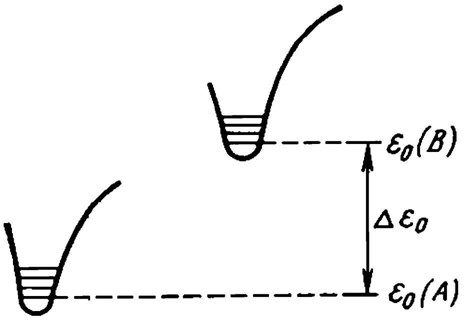

Fig. 6.10. The energy levels of molecules of the reactant and product.

In order to calculate theoretically the equilibrium constant with the aid of relation (6.125), one has to know, along with the value of ΔU_0, the various characteristics of reacting molecules, i.e., masses, vibration frequencies, moments of inertia, symmetry numbers, and electronic states.

The relationship between the equilibrium constant and the partition functions per unit volume, which are defined by (6.124) and which have the dimensions of concentrations, is also widely used in the theory of chemical kinetics—the absolute reaction rate theory.

It may also be noted that in expression (6.125) the heat effect of reaction may be referred not to one mole but to one molecule and, in place of $\Delta U_0/R$ or $\Delta E_0/R$, we may write $\Delta\varepsilon_0/k$.

6.15. Some Values of Energy Level Degeneracy

We have repeatedly written the molecular partition function in the most compact form, taking into account the multiplicity or degeneracy of the energy levels of molecules. Thus, Q is reduced to a form that takes account of the results of application of quantum theory to a study of molecules:

$$Q = g_0 e^{-\varepsilon_0/kT} + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots = \sum_i g_i e^{-\varepsilon_i/kT} \qquad (6.126)$$

where, as before, the summation is over all the possible energy states of molecules. For monatomic molecules the level degeneracy is equal to the multiplicity of the corresponding spectral term*. For example, for atoms of inert gases in the ground electronic state $g_0 = 1$ (the singlet level), and for atoms of alkali metals in the vapour state $g_0 = 2$ (the doublet level). For molecules containing several atoms, the expression for g may become considerably complicated. For instance, for a diatomic molecule with a nondegenerate ground electronic level the total degeneracy is given by the degeneracy of the rotational level and is equal to

$$2J + 1 \qquad (6.127)$$

where J is the so-called rotational quantum number. Since J may assume the values 0, 1, 2, 3, . . ., it follows that only the ground level is nondegenerate. The other levels have degeneracies equal to 3, 5, 7, 9, etc.

In a complex molecule there may also occur vibrational motions of atoms relative to their mean positions. Here we only note that the vibrational levels of all diatomic molecules are nondegenerate.

6.16. Approximate Values of the Partition Function of an Ideal Gas

In a general case, the energy of a molecule of an ideal gas may be represented by the sum of the translational, electronic excitation, vibrational and rotational energies, i.e.,

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{el} + \varepsilon_{vib} + \varepsilon_{rot} \qquad (6.128)$$

In the sum (6.128) the last three terms represent the intramolecular energy and, strictly speaking, they are interrelated—the vibration has an effect on the rotational energy, etc. The translational energy is independent of the other kinds of motion, and vice versa. Therefore, the total energy of a molecule can be split into two independent components, which refer to translational motion and intramolecular states:

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* For the theory of origin of atomic and molecular spectra, the reader is referred to the literature listed at the end of the book (II. Statistical Mechanics and Thermodynamics) and also to Sec. 6.19.

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{intra} \tag{6.129}$$

Accordingly, the molecular partition function can also be expressed in terms of two cofactors:

$$Q = Q_{tr}Q_{intra} \tag{6.130}$$

In the next section we shall describe a method of calculating the translational partition function Q_{tr}. For the quantity Q_{intra} to be determined accurately one must first of all have detailed information on the energy levels of a molecule; this information is mainly obtained by means of the spectroscopic methods of investigation. Second, one must carry out the summation of all the terms of the type $\exp(-\varepsilon_i/kT)$ referring to individual energy levels. This direct summation is the only method reliable over a wide temperature range. It is, however, very laborious and can only be simplified through the use of electronic computers. It is for this reason that resort is often made to approximation methods which give satisfactory results at not too high temperatures.

For example, at a first approximation it is assumed that all the intramolecular forms of energy are also independent of one another*. In such a case, the total molecular partition function may be represented as the product of the sums calculated for the individual forms of energy, i.e.,

$$Q = Q_{tr}Q_{el}Q_{vib}Q_{rot} \tag{6.131}$$

We shall use only the formula of this approximation and therefore in the section that follows we shall be concerned with the determination of various Q_i.

6.17. The Simplest Partition Functions for Individual Types of Motion

The Energy of Electronic Excitation. Let a molecule have the following series of the lowest energy levels for the outer electron shell: $\varepsilon_0 = 0, \varepsilon_1, \varepsilon_2, \ldots$. Here ε_0 is the energy of the unexcited, ground level and is taken as the point of reference; ε_1 and $\varepsilon_2 \ldots$ are, respectively, the energies of the first, second, etc., excited levels. The electronic partition function is written in a general form as

$$Q_{el} = g_0 e^{-\varepsilon_0/kT} + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots \tag{6.132}$$

where $g_0, g_1 \ldots$ are the degeneracies of the corresponding levels. In many cases, however, even the energy of the first excited electronic level is high as compared with the average energy of thermal motion, a measure of which is kT. For instance, ε_1 is often of the order of several (4-5) electron-volts; as for kT, it is approximately equal to 10^{-4} T eV; at room temperature (300°K) it equals 0.03 eV. Therefore, already in the second term the negative exponent may be much greater than unity and the term itself very small. Hence, at not very high temperatures all the terms in the partition function (6.132) may be neglected, except the first one, and the quantity Q_{el} may be assumed to be equal to the degeneracy (multiplicity) of the ground electronic level, i.e.,

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* This approximation is known as the Born-Oppenheimer approximation.

$$Q_{\text{el}} = g_0 \tag{6.133}$$

This factor is usually included in the translational partition function, which is discussed below.

Translational Motion. When calculating the partition function for the translational motion of an ideal gas the molecule is treated as a particle which possesses mass and is capable of moving in space.

The energy of unrestricted translational motion is not quantized in general, i.e., it can change continuously. This feature distinguishes this kind of motion from the other types of motion which are periodic in character—vibration, rotation, etc. Therefore, Q_{tr} should be computed by integration rather than summation. And this is what we shall do. However, we shall first show that translational motion limited in its extent appears to display the properties of periodic motion and its energy may assume only certain discrete values. Let us consider the simplest quantum-mechanical problem—a single free particle moving in a potential box. This problem is usually known as the particle in a box. Imagine a particle, say a gas molecule, moving in a rectangular box of dimensions l_x, l_y and l_z. The properties of the particle-box system are such that the potential energy of the particle, $v(x, y, z)$, inside the box is constant and may be taken to be equal to zero. At the boundaries of the box, however, the potential energy of the particle is assumed to increase to infinity, which means that the particle cannot actually go beyond the boundaries of the box.

In quantum mechanics, there is a postulate that the state of a microscopic system (an electron, atom, or molecule) must be defined by the Schrödinger wave equation:

$$\frac{h^2}{8\pi^2 m} \nabla^2 \psi + (E - v)\psi = 0 \tag{6.134}$$

where ψ is the so-called wave function, the square of which* expresses the density of the probability of finding the particle at a given point in space; the operator ∇^2 ("del squared" or "nabla squared")** signifies the sum of the second partial derivatives of ψ with respect to the coordinates x, y, and z, i.e.,

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* More exactly, the product of complex-conjugate functions.

** This operator is called the Laplacian.—*Tr.*

$$\nabla^2\psi=\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}$$

where m is the mass of the particle; E and v are, respectively, its total and potential energies. According to the formulated condition of the problem of the particle in a box, $v = 0$. Consider a simplified solution of Eq. (6.134), assuming that the particle performs only one-dimensional motion* along the coordinate axis x from 0 to l_x. In this case, Eq. (6.134) becomes

$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi x}{dx^2}+E_x\psi_x=0 \qquad (6.135)$$

The general solution of an equation of this type is known to be a sinusoidal function of the type

$$\psi_x = c\sin(Ax + B) \qquad (6.136)$$

According to what has been said above, ψ_x^2 will determine the probability of finding the particle at point x. From this it follows that ψ_x must be equal to zero at $x = 0$ and at $x = l$, and this is possible if

$$A=\frac{n_x\pi}{l_x} \quad \text{and} \quad B=0$$

where n_x is an integer (1, 2, 3, . . .). Thus, the solution of Eq. (6.135) that satisfies all the conditions specified will be

$$\psi_x=c\sin\left(\frac{n_x\pi}{l_x}x\right) \qquad (6.137)$$

Substituting this solution into the original equation (6.135), we obtain:

$$-\frac{h^2}{8\pi^2 m}\frac{n_x^2\pi^2}{l_x^2}c\sin\left(\frac{n_x\pi}{l_x}x\right)+E_x c\sin\left(\frac{n_x\pi}{l_x}\right)=0$$

or

$$E_x=\frac{h^2}{8ml_x^2}n_x^2 \qquad (6.138)$$

where n_x is a quantum number which determines the allowed energy values for a particle constrained to move in parallel to the x axis. According to Eq. (6.138), E_x may assume only those values which are multiples of $h^2/8\pi l_x^2$ and the constrained one-dimensional translational motion is found to be quantized. Figure 6.11 shows a diagram of energy levels E_x up to $n_x = 4$.

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* The figurative expression occasionally used in such cases is the "bead-string model".

It is in this way that discrete energy levels are defined in more complex systems—an electron interacting with a positively charged nucleus, the vibrational motions of atoms in a molecule, and the rotation of a molecule. As we know, the discrete nature of energy levels in an atom and molecule is reflected in the pattern of emission, absorption, Raman and other spectra. A detailed study of spectra provides information on energy levels.

Returning to translational motion, we note that quite analogous solutions are obtained for the motion in the y and z directions, and by means of summation we can also write the total energy of the particle in a three-dimensional box. However, we shall not do this; we shall only use relation (6.138) for the direct calculation of the partition function of one-dimensional translational motion:

$$Q_{\mathrm{tr}(x)} = \sum_{n=1}^{\infty} e^{-\frac{h^2}{8ml_x^2 \mathrm{k}T} n_x^2} \qquad (6.139)$$

The calculation of this sum is simplified because for gases the factor $h^2/8ml_x^2\mathrm{k}T$ is very small—the energy levels are spaced very closely, and therefore the summation can be replaced, to a sufficient degree of approximation, by integration over n, assuming that it changes not from unity but from zero:

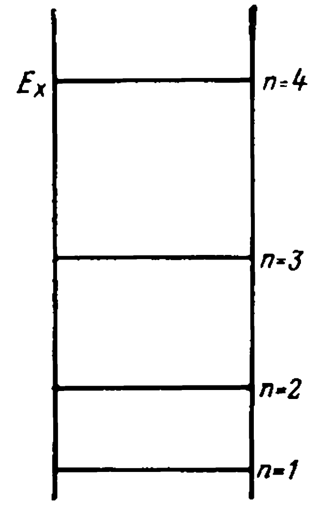

Fig. 6.11. Approximate disposition of energy levels of the restricted (l_x) translational motion of a particle (Equation 6.138).

$$Q_{\mathrm{tr}(x)} = \int_0^{\infty} e^{-\frac{h^2}{8ml_x^2 \mathrm{k}T} n_x^2} dn = \frac{(8m\,\mathrm{k}T)^{1/2}}{h} l_x \int_0^{\infty} e^{-\rho^2} d\rho \qquad (6.140)$$

Here the following substitution is made: $\rho^2 \doteq h^2n^2/8ml_x^2\mathrm{k}T$. The integral in Eq. (6.140) is known to be equal to $\pi^{1/2}/2$. Therefore we obtain the expression for the partition function for one-dimensional translational motion that has been derived in Sec. 6.11 in a somewhat different way:

$$Q_{\mathrm{tr}(x)} = \frac{(2\pi m\,\mathrm{k}T)^{1/2}}{h} l_x \qquad (6.141)$$

Analogous partition functions are obtained for a motion paralleto the other two directions. Since the motions in all the three direcl tions are independent, the total partition function of the translational motion of the particle in a potential box will be given by the product:

$$Q_{\text{tr}} = Q_{\text{tr}(x)}Q_{\text{tr}(y)}Q_{\text{tr}(z)} = \frac{(2\pi m\,\text{k}T)^{3/2}}{h^3}\,l_x l_y l_z$$

or

$$Q_{\text{tr}} = \frac{(2\pi m\,\text{k}T)^{3/2}}{h^3}\,V \tag{6.142}$$

where V is the volume of the box. Formula (6.142) can be used to calculate the translational partition function for a gaseous molecule moving in an ordinary vessel.

Let us, finally, include, in accordance with what has been said above (page 274), the degeneracy of the ground electronic level in the translational partition function:

$$Q_{\text{el. tr}} = g_0\,\frac{(2\pi m\,\text{k}T)^{3/2}}{h^3}\,V \tag{6.143}$$

In calculating the thermodynamic functions for N_{A} molecules, i.e., for one mole, V is taken to mean a molar volume equal to RT/p for an ideal gas.

Vibrational Motion of Atoms in a Molecule (a Harmonic Oscillator). In diatomic molecules there develops a motion associated with the change of internuclear distances—valence vibrations. In more complex molecules there are also possible various modes of deformation vibrations, which lead to a change in bond angles. We shall consider in more detail the vibrations of atoms in a diatomic molecule.

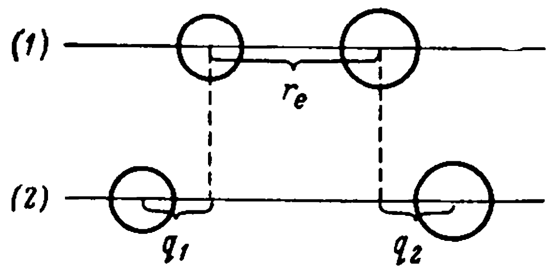

Fig. 6.12. Displacement of atoms in a diatomic molecule relative to the position of equilibrium r_e:

1—position corresponding to the minimum of the potential energy (U); 2—molecule in the "extended" state with an increased potential energy.

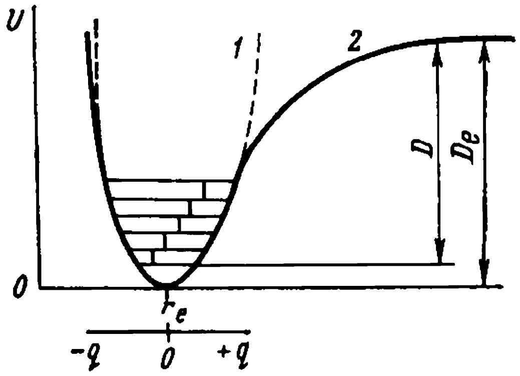

Fig. 6.13. Dependence of the potential energy of a diatomic molecule on the internuclear distance:

1—harmonic approximation; 2—actual dependence; the short vertical lines represent the transitions of the oscillator from one energy state to another; they are displaced relative to each other for the sake of clarity (see Sec. 6.19—the vibrational spectrum).

Figure 6.12 shows a model of a diatomic molecule with an equilibrium internuclear distance r_e. The lower part of this figure shows the displacement of atoms from the equilibrium position by the total amount $q = q_1 + q_2$. The restoring force that arises during the displacement can be regarded, at a first approximation, as being proportional to the displacement or obeying Hooke's law*, i.e., $F(q) = -K_e q$, where K_e is the so-called force constant.

The potential energy of the system will in this case be a quadratic displacement function:

$$U(q) = \frac{1}{2} K_e q^2 \tag{6.144}$$

The dependence of the molecule's potential energy on displacement is expressed by a parabolic curve shown in Fig. 6.13 by a dashed line. The solid line depicts the actual dependence of the molecule's potential energy on the distance between the atoms (internuclear distance) in a diatomic molecule. This curve is described by the Morse empirical function:

$$U = D_e [1 - e^{-a(r-r_e)}]^2$$

Its most significant difference from a parabola consists in that as r increases the quantity U tends to a limit equal to D_e (the spectroscopic dissociation energy). The parabolic function is applicable only at small displacements. The motion of particles that arises under these conditions is a harmonic vibration with the frequency

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K_c}{\mu}} \tag{6.145}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass of the molecule. The instantaneous kinetic energy of the vibrating atoms may be represented in the form:

$$T = \frac{1}{2} \mu \dot{q}^2 \tag{6.146}$$

According to quantum theory, i.e., the solution of the Schrödinger equation with these values of U and μ, the energy of the harmonic oscillator vibrating with frequency ν is equal to

$$\varepsilon_{\text{vib}} = T + U = h\nu \left(v + \frac{1}{2}\right) \tag{6.147}$$

where v is the vibrational quantum number which may assume positive integral values, $v = 0, 1, 2, 3, \ldots$.

Figure 6.13 shows the equidistant levels of the total vibrational energy of the molecule as a harmonic oscillator.

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* It is therefore called the quasi-elastic force.

The partition function for the vibrational mode under discussion is written as*

$$Q'_{\text{vib}}=\sum_{v=0}^{v=\infty} e^{-h\nu\left(v+\frac{1}{2}\right)/kT}=e^{-\frac{h\nu}{2kT}}\left(1+e^{-\frac{h\nu}{kT}}+e^{-\frac{2h\nu}{kT}}+\dots\right) \quad (6.148)$$

From this equation it is seen that enclosed in parentheses is a geometric progression series of the type

$$1+x+x^2+x^3+\dots=(1-x)^{-1} \quad (6.149)$$

Therefore, the vibrational partition function is given by

$$Q'_{\text{vib}}=e^{-\frac{h\nu}{2kT}}\left(1-e^{-\frac{h\nu}{kT}}\right)^{-1} \quad (6.150)$$

The quantity $h\nu/2$ is the lowest value of vibrational energy corresponding to $v=0$; it is the zero-point vibrational energy. This quantity is often included in the total zero (i.e., at absolute zero) energy of the molecule, and the vibrational energy is counted off from this lowest level (see Sec. 6.14). In this case, the vibrational partition function takes the form

$$Q_{\text{vib}}=\left(1-e^{-\frac{h\nu}{kT}}\right)^{-1} \quad (6.151)$$

From the foregoing it follows that the formula obtained applies only to a harmonically oscillating diatomic molecule, i.e., an ideal model. As a matter of fact, as q (or r) increases the potential energy tends not to infinity, as follows from Eq. (6.144), but to a limit D_e called the *spectroscopic dissociation energy*. The energy actually consumed for the dissociation of a molecule, which is in the zero-point vibrational level, is equal to D (the chemical energy of dissociation). The actual dependence $U(q)=f(q)$ is fairly well described by the above-mentioned Morse function, which contains $q=r-r_e$ in the exponent. Nevertheless, the results of the calculation of the sum (6.151) differ little (especially for not too high temperatures) from those obtained by the more accurate method of direct summation over the approaching levels of anharmonic oscillators.

Let us now consider the problem of the equilibrium distribution of diatomic molecules among the vibrational energy levels or, what is the same thing, the population of the vibrational levels. This plays a substantial role in studying the effect of vibrational motions on their contribution to the thermodynamic functions. Since the vibrational levels of a diatomic molecule are nondegenerate**, the

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* As has already been pointed out, the vibrational energy levels of a diatomic molecule are nondegenerate ($g_i=1$).

** This may be interpreted as follows: the vibration occurs in a single direction—along the line connecting the centres of the atoms.

Boltzmann distribution law is written in this case in the simplest form (6.76):

$$N_{i,\,\mathrm{vib}}=N\frac{e^{-\varepsilon_{\mathrm{vib}}/kT}}{Q_{\mathrm{vib}}} \qquad (6.152)$$

where N is the total number of molecules (the total occupation number); $N_{i,\,\mathrm{vib}}$ is the number of molecules that occupy a given vibrational level. The level energy $\varepsilon_{\mathrm{vib}}$ and Q_{vib} are defined by relations (6.147) and (6.151), respectively. Figure 6.14 shows the distribution curves or the relative* population of the vibrational levels of the chlorine and iodine molecules at 300°K. It is essential that in the absence of degeneracy the population is governed exclusively by the exponential factor and therefore the lowest-energy level has the largest population. Here we can recall the nature of the distribution of molecules by a single velocity component (see Fig. 6.3) where the energy levels are also nondegenerate.

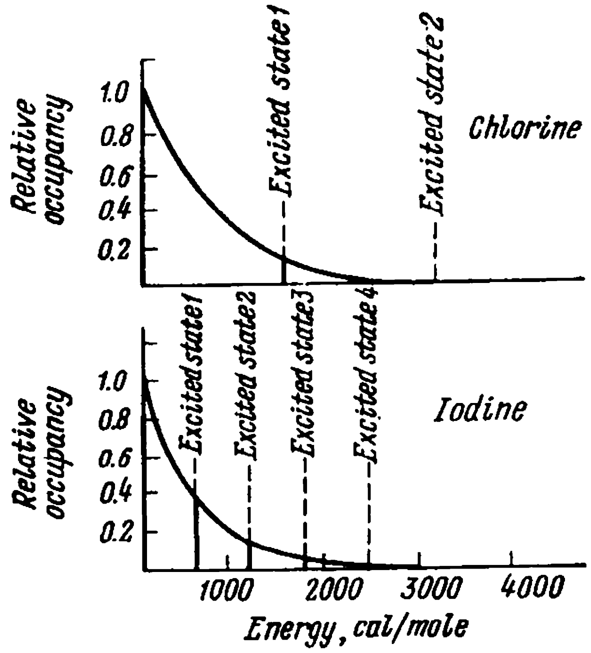

Fig. 6.14. Relative occupancy of the vibrational levels of the molecules Cl_2 and I_2 at 300°K.

The iodine molecule vibrates at relatively low frequencies** and the spacing of the energy levels is relatively small (see Fig. 6.14). Because of this, even at 300°K the vibrational levels of iodine are appreciably populated. Thus, the population of the first level ($v = 1$) is about one-third of the population of the lowest-energy level. In contrast to this, the vibrations of the chlorine molecule which occur at high frequencies are excited only slightly. The second energy level ($v = 2$) is not practically occupied and the population of the first level is about one-tenth of the population of the lowest-energy level (Fig. 6.14). What has been said is most typical of simple molecules, but in polyatomic molecules the situation may be substantially different because of the realization of several vibrations with frequencies as low as or even lower than in the case of iodine. Nevertheless, we may assume, to a first approximation, that at room temperature molecular vibrations make a minor contribution to the thermodynamic functions (entropy, etc.).

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* That is, referred to the "population" of the zero level.

** See formula (6.145)—the force constant of I_2 is smaller and the reduced mass greater than those for the chlorine molecule.

Calculation of the Vibrational Partition Function of a Polyatomic Molecule. This task is incomparably more formidable than the previous one. In practice, one often resorts to the zeroth-approximation method which yields satisfactory results at moderate temperatures. The method makes allowance for the existence in a polyatomic molecule of several (sometimes, many) modes of harmonic oscillation with different frequencies, the energy of each one being expressed by a formula of the type (6.147). A nonlinear molecule consisting of m atoms has $3m - 6$ vibrational modes. For a linear molecule, because of the number of rotational degrees of freedom being reduced by unity, the number of vibrational modes is $3m - 5$. If a molecule has a degree of freedom of internal rotation (for example, of methyl groups about the bond line in ethane), the number of vibrational modes falls down to $3m - 7$. In a general case, when the number of vibrational modes is $3m - x$, the partition function is approximately written in the following form:

$$Q_{\text{vib}} \approx \prod_{i=1}^{3m-x} \left(1 - e^{-\frac{h\nu_i}{kT}}\right)^{-1} \tag{6.153}$$

Here the product includes analogous factors for all modes of vibration.

Rotation of a Molecule (a Rigid Rotator). According to quantum-mechanical calculations, the rotational energy of a diatomic molecule with the internuclear distance r_e being unchanged (a rigid rotator) is given by the relation

$$\varepsilon_{\text{rot}} = \frac{h^2}{8\pi^2 I} J (J+1) \tag{6.154}$$

where I is the moment of inertia defined by

$$I = r_e^2 \frac{m_1 m_2}{m_1 + m_2} \tag{6.155}$$

and J is the rotational quantum number which takes the values 0, 1, 2, 3, ... To each rotational energy level (the value of the number J) there corresponds the degeneracy $2J + 1$. Therefore, the partition function is written in the form

$$Q'_{\text{rot}} = \sum_{0}^{\infty} (2J+1) e^{-\frac{h^2 J (J+1)}{8\pi^2 I kT}} = \sum (2J+1) e^{-bJ(J+1)} \tag{6.156}$$

Frequently, in the case of sufficiently heavy molecules and not too low temperatures, that is, when b is small, the direct summation is replaced by integration. If z is substituted for $J(J+1) = J^2 + J$, then

$$dz = (2J + 1)\,dJ \quad \text{and} \quad Q'_{\text{rot}} = \int_0^\infty e^{-bz}\,dz = 1/b$$

The integral equals $1/b$. Hence, the partition function

$$Q'_{\text{rot}} = \frac{8\pi^2 IkT}{h^2} \tag{6.157}$$

Expression (6.157) is not complete. Usually, it also contains factors corresponding to the nuclear spin degeneracy caused by nuclear spins (known as the spin factor).

A distinction is made between molecules having identical and different nuclei. The former give rise to so-called *ortho-* and *para-*states. We shall consider this case in more detail. The spin quantum number of each nucleus is i. Two identical spins combine in $2i + 1$ ways; the net nuclear spin of the molecule may assume the values $2i, 2i - 1, 2i - 2, 2i - 3 \ldots 2, 1, 0$. The first, third, fifth, etc., values correspond in quantum mechanics to symmetric eigenfunctions or symmetric states. The second, fourth, sixth, etc., values correspond to antisymmetric states. The general expression for the resultant spin is

$$t = 2i - n \tag{6.158}$$

where the lowest value of n is 0 and the largest value $2i$. The symmetric states (n is an even integer or 0) are also called *ortho*-states. The antisymmetric states (n is an odd integer) are termed *para*-states. For each value of the net spin t there are possible $2t + 1$ orientations. Since the quantity t itself is equal to $2i - n$, the degeneracy, i.e., the number of equi-energy levels corresponding to a combination of two nuclear spins, is $2(2i - n) + 1$. Thus, the total degeneracy of *ortho*-states is

$$g_{\text{nuc}\,(ortho)} = \sum_{n=0,2,4,\ldots,2i} [2(2i - n) + 1] = (i + 1)(2i + 1) \tag{6.159}$$

and the degeneracy of *para*-states

$$g_{\text{nuc}\,(para)} = \sum_{n=1,3,5,\ldots,2i-1} [2(2i - n) + 1] = i(2i + 1) \tag{6.160}$$

When writing the total rotational partition function for a molecule with identical nuclei it is necessary to know which values of rotational quantum numbers (even or odd) correspond to *ortho-* and which to *para*-states. This is solved, for example, by studying band spectra. The summation must be carried out over *ortho-* and *para*-states separately:

$$Q_{\text{rot}} = g'_{\text{nuc}} \sum_{0,2\ldots} (2J+1)\, e^{-bJ(J+1)} + g''_{\text{nuc}} \sum_{1,3\ldots} (2J+1)\, e^{-bJ(J+1)} \qquad (6.161)$$

where g'_{nuc} and g''_{nuc} are given by relations (6.159) and (6.160). Let us assume, as before, that b is small. Then, the summation in Eq. (6.161) can be replaced by integration and we can show that each sum is equal to $1/2b$*.

Hence,

$$Q_{\text{rot}} = (g'_{\text{nuc}} + g''_{\text{nuc}}) \frac{1}{2b} \qquad (6.162)$$

But since, according to Eqs. (6.159) and (6.160), $g'_{\text{nuc}} + g''_{\text{nuc}} = (2i+1)^2$, the rotational partition function for a symmetric molecule can be written as

$$Q_{\text{rot}} = (2i+1)^2 \frac{8\pi^2 IkT}{2h^2} \qquad (6.163)$$

In an unsymmetrical molecule, i.e., one consisting of different nuclei, there are no *ortho-* and *para*-states. If the nuclear spins are, respectively, equal to i and i', then, taking into account the number of possible orientations for each of them, we find that the spin factor *is equal to* $(2i+1)(2i'+1)$. The calculation of the rotational partition function will not differ from the calculation of the sum in (6.157). Thus, for an unsymmetrical molecule we have

$$Q_{\text{rot}} = (2i+1)(2i'+1) \frac{8\pi^2 IkT}{h^2} \qquad (6.164)$$

Comparing relations (6.163) and (6.164), we see that they differ by the presence or absence of 2 in the denominator. The number 2 is considered to express the symmetry of molecules, i.e., the number of indistinguishable positions occupied by the molecule upon rotation by 360°. In a general form, the symmetry number is denoted as σ. We can now write the final expression for the rotational partition function of a diatomic molecule:

$$Q_{\text{rot}} = (2i+1)(2i'+1) \frac{8\pi^2 IkT}{\sigma h^2} = g_{\text{nuc}} \frac{8\pi^2 IkT}{\sigma h^2} \qquad (6.165)$$

which applies equally well to symmetrical and unsymmetrical molecules. For symmetrical molecules i and i' are the same and Eq. (6.165) changes to (6.163), and for unsymmetrical molecules $\sigma = 1$, whence Eq. (6.164) is obtained.

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* Each sum is twice less than the sum (6.156), which is equal to $1/b$, since the summation here is over an energy level.

Let us consider the effect of the degeneracy of rotational levels on the equilibrium distribution of molecules or on the population of rotational levels. The Boltzmann distribution law should in this case be used in the form (6.76), i.e.,

$$N_{i\,(\mathrm{rot})} = N\frac{g_i e^{-\varepsilon_{\mathrm{rot}}/\mathrm{k}T}}{Q_{\mathrm{rot}}} = N\frac{(2J+1)\,e^{-bJ(J+1)}}{Q_{\mathrm{rot}}} \tag{6.166}$$

where, as before, J is the rotational quantum number and b has the previous value equal to $h^2/8\pi^2 I\mathrm{k}T$, and Q_{rot} is defined by relation (6.165). Figure 6.15 shows the relative populations of the rotational levels of the hydrogen chloride molecule at 300°K. Here, first, the levels themselves are arranged considerably nearer to one another than the earlier considered vibrational levels and, second, a substantial role in the equilibrium distribution of molecules is played by the level degeneracy equal to $2J+1$. In Fig. 6.15 the curve *1* shows how the relative population would be changed in the absence of level degeneracy if the distribution depended only on the exponential cofactor $\exp\left(-\varepsilon_{\mathrm{rot}}/\mathrm{k}T\right)$. The curve *2* corresponds to the actual distribution of molecules with the degeneracy equal to $2J+1$ being taken into account. Here, just as in the case of three-dimensional translational motion (see Sec. 6.11) we can say that each rotation defined by the quantum number J is capable of orientation in $2J+1$ directions. In this sense, the factor $2J+1$ in formula (6.166) can be compared with the factor $4\pi c^2\,dc$ in the Maxwell equation (6.90). As can be seen from Fig. 6.15, the level with $J=3$ has an approximately four-fold population as compared with the unexcited level. At small values of J the magnitude of the pre-exponential factor clearly predominates. Even the state with $J=6$ has a greater population than at $J=0$. According to what has been said, rotational states introduce a considerable disorder into the energy distribution even at low temperatures and, hence, they make a substantial contribution to the thermodynamic functions: heat capacity, entropy, etc.

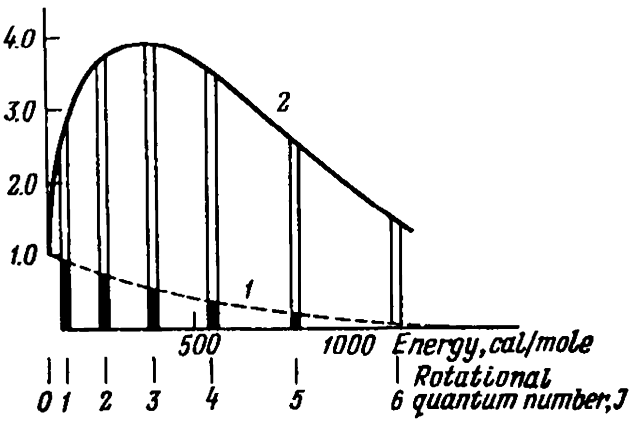

Fig. 6.15. Relative population of the rotational states in HCl molecules at 300°K:

Curve *1*—distribution without account of the degeneracy (statistical weight) of energy levels; curve *2*—actual distribution with account of the level degeneracy $2J+1$.

The Rotational Partition Function of Polyatomic Molecules. For a nonlinear polyatomic molecule with three identical moments of inertia (for example, methane or its symmetrical derivatives) the rotational partition function is given by

$$Q_{\text{rot}} = g_{\text{nuc}} \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 I kT}{h^2} \right)^{3/2} \tag{6.167}$$

The spin factor is found by multiplying terms of the type $(2i + 1)$ through for each nucleus, and the symmetry number is $\sigma = 12$.

More frequent are examples of molecules in which two of the three moments of inertia are equal. In such cases, we can obtain only an approximate expression for the partition function, namely:

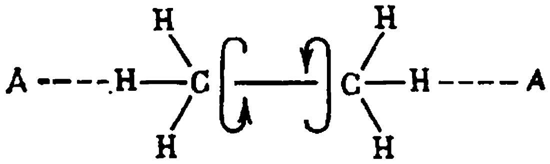

Fig. 6.16. Internal rotation in the ethane molecule. *AA*—axis of rotation.

$$Q_{\text{rot}} = g_{\text{nuc}} \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} I_A I_C^{1/2} \tag{6.168}$$

The partition function for a molecule with three different moments of inertia is written in an analogous manner:

$$Q_{\text{rot}} = g_{\text{nuc}} \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A I_B I_C)^{1/2} \tag{6.169}$$

Thus, in order to calculate the partition function by using formula (6.169) there is no need to know the individual values of moments of inertia. Methods have therefore been developed for the direct determination of the product $(I_A I_B I_C)$.

In concluding, we may add that in calculations involving chemistry (the determination of equilibrium constants and thermodynamic functions for these purposes) the spin factor in Eqs. (6.165), (6.167) and (6.169) may be dropped out since the nuclear state does not change in a chemical reaction in the absence of *ortho-para* conversions.

Internal Rotation: Free and Hindered Rotations. A molecule can exhibit one more kind of motion—the rotation of one part of the molecule relative to the other. An example of such internal motion is the rotation of the methyl groups in the ethane molecule about the axis passing through the carbon atoms (Fig. 6.16). The methyl groups may be regarded as symmetric tops with two equal moments of inertia relative to the axes perpendicular to the principal axis of rotation of the top. Often in a molecule a rigid framework may be distinguished, with which one or more rigid tops are connected.

The possibility of internal rotation must be taken into account in setting up the total partition function—it reduces the number of vibrational degrees of freedom. Sometimes, internal rotation may be treated, to a first approximation, as a free rotation, i.e., one in which no energy barrier has to be surmounted.

Let us introduce the so-called reduced moment of inertia:

$$I_m = \frac{I_1 I_2}{I_1 + I_2} \tag{6.170}$$

where I_1 and I_2 are the moments of inertia of two parts of the molecule rotating relative to each other. It can be shown that the partition function of internal rotation is given by the relation

$$Q_{\text{fr}} = \frac{(8\pi^3 I_m kT)^{1/2}}{h} \tag{6.171}$$

Here, however, no account is taken of the symmetry of the molecule. This can be done by two methods. In one method, the total symmetry number is inserted into the expression for the partition function derived for external rotation [for example, into formula (6.169)]. In the other, the symmetry number is split into two parts: one for the external rotation of, so to say, a rigid molecule which does not display internal rotation; the other component refers only to those groups which are rotating inside the molecule. The second method is used more frequently. So, the partition function for each freely rotating group will be written as

$$Q_{\text{fr}} = \frac{(8\pi^3 I kT)^{1/2}}{\sigma_i h} \tag{6.172}$$

For instance, for ethane the total symmetry number is 18 and it can be included in the expression for the rotational partition function of the molecule as a whole. In the second method, however, this number (18) is regarded as the product of two cofactors. One of them, which is equal to 6, characterizes the rotation of the molecule as a whole: upon rotation about the C—C axis the molecule occupies three indistinguishable positions, each of which can be realized twice upon rotation by 360° about the axis perpendicular to the C—C bond. The symmetry number of internal rotation $\sigma = 3$ since upon rotation of the methyl group about the C—C axis, as shown in Fig. 6.16, it will also occupy three indistinguishable positions. Since the indistinguishable positions can combine in any way, there will be 18 such positions.

In a general case, a molecule can have S rotational degrees of freedom: three of them refer to external rotation and (S—3) to internal rotation. A rather laborious computation based on the classical method and involving integration over S coordinates and S

momenta yields a result which may be represented in the form:

$$Q_{\text{rot}} = \left\{ \frac{\pi^{1/2}}{\sigma_e} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A I_B I_C)^{1/2} \right\} \left\{ \prod_{i=1}^{S-3} \frac{(8\pi^3 I_k kT)^{1/2}}{\sigma_i h} \right\} \qquad (6.173)$$

In this expression, I_k are moments of inertia of $(S-3)$ groups which are assumed to rotate freely inside the molecule about the bonds linking these groups to the rigid framework of the molecule; σ_e is the symmetry number of external rotation and σ_i is the symmetry number of internal modes of rotation.

In the above formula the first term in braces coincides, if the nuclear spin factor which does not appear in Eq. (6.173) is disregarded, with formula (6.169) which expresses the partition function of only the external rotation of a nonlinear molecule with three different moments of inertia. The second term in braces includes the product of $(S - 3)$ cofactors, which are analogous to those in Eq. (6.172) and correspond to $(S - 3)$ degrees of freedom of internal rotation. According to the result obtained, we can separate, at a first approximation, the external rotation from the internal rotation and the latter can also be represented in the form of cofactors corresponding to the rotation of individual groups. Formula (6.173) can be written in the following abbreviated form:

$$Q_{\text{rot}} = Q_{\text{ex}} \prod_{i=1}^{S-3} Q_{\text{fr}} \qquad (6.174)$$

It should be noted that I_m in formula (6.171) differs from I_k in formula (6.173): the former represents the reduced moment of inertia and the latter the moments of individual rotating groups.

It should be remarked that free internal rotation is encountered rather seldom. One of the few examples is the rotation of atomic groups in dimethylcadmium $H_3C—Cd—CH_3$. In this compound, the groups are separated by a relatively large distance—by two Cd—C distances instead of one C—C distance in ethane. The numerical data given below confirm the absence of hindered rotation.

The entropy of dimethylcadmium, cal/deg·mole

Translation plus overall rotation	60.66
Vibration	8.76
Free internal rotation	2.93
Total, calculated	72.35
Total, experimental (according to the . . . third law)	72.40 ± 0.20

The agreement between the entropy calculated statistically and the entropy determined experimentally on the basis of calorimetric data is very good, as can be seen from the data given above.

Hindered Rotation. The entropy value calculated on the assumption of free rotation in the molecules of ethane, propane, butane, tetramethylmethane, etc., has been found to be somewhat higher than the entropy found on the basis of calorimetric measurements. This has led to the supposition that internal rotation is not completely free; a certain energy barrier has to be surmounted—in the cases listed above the energy barrier to rotation is not high (2-3 kcal/mole).

The essence of the matter can most simply be understood by reference to the bipyramidal ethane molecule ($H_3C—CH_3$). Rotation is hindered (or retarded) due to the repulsions between the hydrogen atoms of the two methyl groups. This force of repulsion is at a maximum when the hydrogen atoms in the two methyl groups oppose one another and at a minimum when one group rotates about the other at an angle of $\pi/3$ (Fig. 6.17). The maximum value is again reached on rotation by another $(1/3)\pi$ angle. The symmetry of the groups requires that equal maxima alternate with equal minima on rotation by 360°. The potential function can be expanded into a Fourier series but, as has been found, the first two terms give a fairly good approximation:

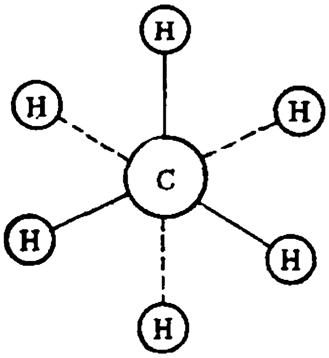

Fig. 6.17. Rotation of methyl groups in ethane (the position of hydrogen atoms correspond to the potential energy minimum).

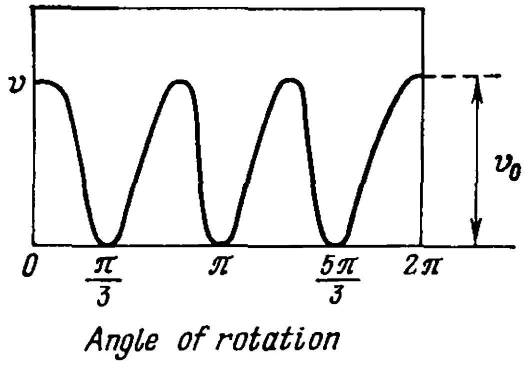

Fig. 6.18. Dependence of the potential energy on the angle of rotation of the methyl group in ethane.

$$v = c_0 + c_1 \cos n\varphi + \dots = \frac{1}{2} v_0 (1 - \cos n\varphi) = v_0 \sin^2 \left(\frac{n\varphi}{2}\right) \tag{6.175}$$

According to the notation of the potential given in the second line, it vanishes at $\varphi = 0$; v_0 corresponds to the largest value of the potential; n is the number of equivalent positions upon rotation of the group by 360°. If all n positions are equivalent, then n coincides with the symmetry number σ_i and the potential can be represented in the form

$$v = v_0 (1 - \cos \sigma_i \varphi) \tag{6.176}$$

Figure 6.18 presents this dependence graphically for ethane. It is seen that equal maxima and minima alternate through every $(2/3)\pi$ in accordance with $\sigma_i = 3$. Equation (6.175) could be used for the solution of the quantum-mechanical problem by means of the Schrödinger equation. In this case, however, no sufficiently simple expression obtains for energy levels and the calculation of the partition function is complicated. A general treatment of the problem is beyond the scope of this book. We shall confine ourselves to the statement that, as has been shown by Pitzer, the contribution of internal rotation to the thermodynamic functions can be tabulated in the form of functions of two properly chosen variables. For example, use may be made of the ratio of the potential barrier height to the thermal energy, i.e., v_0/kT, and the inverse of the rotational partition function for rotation which is assumed to be free, $1/Q_{\text{fr}}$ *. Such tables can also be used for the solution of the inverse problem—if the contribution of hindered internal rotation to some thermodynamic function (say, the entropy) is known, one can find the potential barrier height.

6.18. Calculation of the Thermodynamic Properties of Monatomic and Diatomic Ideal Gases

As an example of the use of the formulas of statistical thermodynamics derived in the preceding sections, let us consider the calculation of some thermodynamic properties of monatomic and diatomic gases. In monatomic gases, at not too high temperatures the total energy is determined by translational motion alone. The electronic levels are often arranged high and are not excited: the corresponding partition function is g_0, i.e., is represented by the degeneracy of the ground electronic state**. The complete partition function is specified by formula (6.143), i.e.,

$$Q_{\text{el. tr}} = g_0 \frac{(2\pi mkT)^{3/2}}{h^3} V \tag{6.177}$$

If we agree upon calculating per one mole of an ideal gas, then V will correspond to the molar volume since it is exactly in this volume that each molecule of the gas can move; then $\bar{v} = RT/p$.

Let us calculate the energy of a monatomic gas from relation (6.110):

$$U - U_0 = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v \tag{6.178}$$

But, according to Eq. (6.177), if v is constant, then the temperature in Q depends on the temperature itself. Therefore, by writing the

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* Tables of heat capacities, enthalpies, Gibbs free energies and entropies can be found in: G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill Book Company, New York, 1961.

** However, with relatively low-lying excited electronic levels ε_1, ε_2 ... the electronic partition function must be written fully according to Eq. (6.126), i.e.,

$$Q_{\text{el}} = g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots$$

logarithm of the partition function in the form

$$\ln Q = \ln C + \frac{3}{2} \ln T$$

where C incorporates all the temperature-independent quantities, we find that

$$\left(\frac{\partial \ln Q}{\partial T}\right)_v = \frac{3}{2}\frac{1}{T} \tag{6.179}$$

and

$$U - U_0 = \frac{3}{2} RT \tag{6.180}$$

This energy value coincides with the energy value known for a monatomic gas in the elementary kinetic theory of gases. Differentiating Eq. (6.180) with respect to temperature, we obtain the well-known result:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{3}{2} R$$

The enthalpy and heat capacity at constant pressure can be calculated by various methods. For instance, we can use relation (6.111):

$$H_T - H_0 = RT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_p \tag{6.181}$$

In this case it is expedient to define the partition function as follows:

$$Q = g_0 \frac{(2\pi m kT)^{3/2}}{h^3} \frac{RT}{p}$$

and

$$\ln Q = \ln C' + \frac{5}{2} \ln T \tag{6.182}$$

Substitution of Eq. (6.182) into Eq. (6.181) yields

$$H_T - H_0 = \frac{5}{2} RT \tag{6.183}$$

Hence,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{5}{2} R$$

The same values can be obtained in a simpler way, by adding $pv = RT$ to the internal energy and R to the heat capacity C_v.

Let us now compute the *entropy of a monatomic gas*. In accordance with Eqs. (6.117) and (6.143) we have:

$$S_T = R \left\{ \ln g_0 \frac{(2\pi m kT)^{3/2}}{h^3} \frac{kT}{p} + \frac{5}{2} \right\} \tag{6.184}$$

Replacing here p, dynes/cm^2, by the pressure in atmospheres from the relation p, dynes/cm^2 = 1.0132×10^6 p, atm, and introducing the molar mass from $m = M/N_A$, where N_A is Avogadro's number.

we find

$$S_T = R\ln g_0 + \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln p_{\mathrm{atm}} + $$
$$+ R\left\{\ln\left(\frac{2\pi \mathrm{k}}{N_A h^2}\right)^{3/2}\frac{\mathrm{k}}{1.0132\times 10^6} + \frac{5}{2}\right\}$$

Or, calculating the constant in braces,

$$S_T = R\ln g_0 + \frac{3}{2}R\ln M + \frac{5}{2}R\ln T -$$
$$- R\ln p_{\mathrm{atm}} - 2.315\ \mathrm{cal/deg\cdot mole} \qquad (6.185)$$

Relation (6.185) is known as the Sackur-Tetrode equation, which was derived originally in a different way. In Table 6.2 the results of calculations from this formula for a few monatomic gases are compared with the entropies found on the basis of the third law of thermodynamics (see Chapter 3). As can be seen from Table 6.2, the agreement between the entropy values found by the two methods is very good and is within the limits of accuracy of calorimetric data. It may be supposed that the data found with the aid of formula (6.185) are in some cases more accurate than the calorimetric data.

TABLE 6.2. **The Entropies of Monatomic Gases, cal/deg·mole**

Substance	Calorimetric data	Data calculated from formula (6.185)
Ne	35.01 ± 0.10	34.95 ± 0.01
Ar	36.95 ± 0.2	36.99 ± 0.01
Kr	39.17 ± 0.1	39.20 ± 0.01
Xe	40.7 ± 0.3	40.54 ± 0.01

If we put $p = 1$ in expression (6.185), the result will express the entropy of a gas in its standard state, i.e.,

$$S_T^\circ = R\left(\ln g_0 + \frac{3}{2}\ln M + \frac{5}{2}\ln T\right) - 2.315\ \mathrm{cal/deg\cdot mole} \qquad (6.186)$$

Subtracting the product TS° (6.186) from $H_T - H_0$ (6.183) and dividing through by temperature, we obtain the so-called reduced Gibbs free energy*:

$$\Phi_T = -\frac{G_T^\circ - H_0^\circ}{T} = R\ln g_0 + \frac{3}{2}R\ln M +$$
$$+\frac{5}{2}R\ln T - 7.283\ \mathrm{cal/deg\cdot mole} \qquad (6.187)$$

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* The reduced Gibbs free energy is also called the free-energy function. In writing this function one takes into account that enthalpy values are independent of the choice of the standard state.

This expression can be obtained directly from the molecular partition function through the use of Eq. (6.119), i.e.,

$$\Phi_T = -\frac{G_T^\circ - H_0^\circ}{T} = R \ln \frac{Q}{N_A} \tag{6.188}$$

Thus, the reduced Gibbs free energy is computed directly from the molecular partition function; it plays an important role in modern thermodynamics and its values for various substances are usually tabulated.*

In American works and handbooks, use is made of a somewhat different expression for the reduced Gibbs free energy, based on H_{298}° rather than H_0°, i.e.,

$$\Phi' = -\frac{G_T^\circ - H_{298}^\circ}{T} \tag{6.189}$$

The values of Φ' can be found by combining Φ with the value of $(H_{298}^\circ - H_0^\circ)$, which is calculated from relation (6.111), i.e.,

$$\Phi_T' = \Phi_T + \frac{H_{298}^\circ - H_0^\circ}{T} = -\frac{G_T^\circ - H_{298}^\circ}{T} \tag{6.190}$$

This function is convenient for the calculation of the ΔG_T° of reaction or of the equilibrium constant from tabulated values of Φ_T' and the heat of reaction at a temperature of 298.15°K:

$$-\frac{\Delta G_T^\circ}{T} = \Delta\Phi_T' - \frac{\Delta H_{298}^\circ}{T} = R \ln K_p \tag{6.191}$$

The last equality is valid only for an ideal gas system. It should be noted that the value of Φ_{298}' is equal to the *standard entropy* of a substance, S_{298}°.

Let us now turn our attention to diatomic and some polyatomic gases. Note that, in accordance with the factorization of the total partition function into cofactors, the thermodynamic properties can be represented as the sum of the corresponding components. For instance, the heat capacity and entropy

$$C_v = C_{v\,(\mathrm{el.\,tr})} + C_{v\,(\mathrm{vib})} + C_{v\,(\mathrm{rot})}$$

$$S = S_{(\mathrm{el.\,tr})} + S_{(\mathrm{vib})} + S_{(\mathrm{rot})}$$

If we now calculate the heat capacities** of some gases from the general formula for C_v, (6.113) and the values for the individual partition functions, the following picture will obtain. The translational component in all cases is equal to $3/2R$ = 2.98 cal/mole, as follows from the principle of equal distribution of energy, according to which there is $1/2RT$ of energy and $1/2R$ of heat capacity per degree of freedom. This principle is also justified in rotational motion. For diatomic molecules there are two rotational degrees of freedom, and the corresponding contribution of rotation to the heat capacity is equal to $R \approx 1.99$ cal/deg·mole. This means that at 300°K the rotational motion is excited and makes a contribution to the absorption of energy with increasing temperature corresponding to the random energy distribution among molecules (see Fig. 6.15). At this temperature in HCl the maximum population is in the third excited rotational level ($J = 3$).

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* See, for example, *Thermodynamic Properties of Individual Substances*, volumes I and II, Izd. Akad. Nauk SSSR, Moscow, 1962.

** For this to be done, one must know the fundamental vibrational frequencies and also the moments of inertia of molecules and symmetry numbers.

The situation is different with vibrational motions. In molecules with considerable vibrational frequencies, say HCl, N_2, O_2, H_2, the energy of even the first vibrational state equal to $1\frac{1}{2}h\nu$ is great as compared with kT; therefore the Boltzmann factor $\exp(-\varepsilon_{\text{vib}}/kT)$ is small and, hence, the energy absorption for vibrations is also small. Thus, for HCl the vibrational component of heat capacity is equal to only 0.0004 cal/deg·mole. For chlorine this component is already substantial and for iodine it is even greater. In this connection, let us return to Fig. 6.14, which shows the population of vibrational levels for the Cl_2 and I_2 molecules. It is characteristic that the vibrational heat capacity for CCl_4 is considerably larger than for CH_4 since vibrations are excited more readily in CCl_4. This is accounted for by the fact that the vibrational frequencies and energies are lower for heavier chlorine atoms. In ethane the vibrational heat capacity is greater than in methane (in ethane there are more vibrational degrees of freedom with lower frequencies) but lower than in CCl_4.

Let us now determine the *molar entropy of a diatomic ideal gas*. First, according to the Sackur-Tetrode formula (6.185), we find the electronic and translational components $S_{\text{el. tr}}$:

$$S_{\text{el. tr}} = R\ln g_0 + \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln p_{\text{atm}} - 2.315\ \text{cal/deg·mole} \qquad (6.192)$$

This formula was used earlier for the calculation of the total entropy of a monatomic gas at moderate temperatures, i.e., with molecules being electronically unexcited. Further, according to Eqs. (6.117) and (6.151),

$$S_{\text{vib}} = R\left\{\frac{h\nu}{kT}(e^{h\nu/kT} - 1)^{-1} + \ln(1 - e^{-h\nu/kT})^{-1}\right\} \qquad (6.193)$$

At moderate temperatures, when a quantum of vibrational energy is usually greater than kT, formula (6.193) can be simplified by neglecting $\exp(-h\nu/kT)$ as compared with unity and by neglecting unity as compared with exp $(h\nu/kT)$:

$$S_{\mathrm{vib}} = R\left(\frac{h\nu}{kT}\right)e^{-h\nu/kT} \tag{6.194}$$

Finally, according to Eq. (6.117) and formula (6.165), the latter being used without account taken of g_{nuc}, we obtain:

$$S_{\mathrm{vib}} = R\left\{\ln\left(\frac{8\pi^2IkT}{\sigma h^2}\right)+1\right\} = R\ln\frac{IT}{\sigma} + \\ + 177.676\ \mathrm{cal/deg\cdot mole} \tag{6.195}$$

Let us calculate the entropy of nitrogen which is in its standard state at 1 atm and 298.15°K if $M = 28$, $g_0 = 1$ and $R = 1.987$ cal/mole·deg. From Eq. (6.185) it follows that $S^{\circ}_{298\,(\mathrm{el.\,tr})} = 35.95$ eu.

With the vibrational frequency of the nitrogen molecule $\omega_e = 2359.60\ \mathrm{cm}^{-1}$ the vibrational component of its entropy is found to be vanishingly small at a given temperature, i.e., $S_{298\,(\mathrm{vib})} \approx 0$. In this connection, it should be remarked that in general with vibrations that arise along the strong bonds of relatively light atoms and have high frequencies, the corresponding contributions to the total entropy and other thermodynamic properties are negligibly small. More important are weak vibrations, say deformation vibrations associated with the change of bond angles.

The moment of inertia of the nitrogen molecule is $I = 14.01 \times 10^{-40}\ \mathrm{g\cdot cm^2}$ and the symmetry number is $\sigma = 2$. Hence according to formula (6.195),

$$S_{298\,(\mathrm{rot})} = 9.8\ \mathrm{eu}$$

Comparing the calculated entropy terms, we can see that the largest contribution to the total entropy is made by translational motion, the smaller by rotation, and the smallest by vibration.

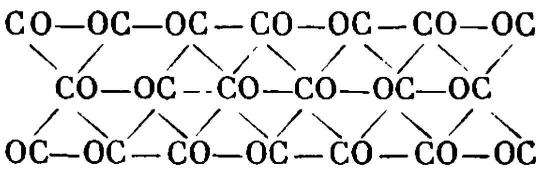
The total entropy of nitrogen in its standard state is equal, according to calculations from the molecular constants, to

$$S^{\circ}_{298} = S_{\mathrm{el.tr}} + S_{\mathrm{vib}} + S_{\mathrm{rot}} = 45.79\ \mathrm{eu}$$

This value is in good agreement with the value obtained calorimetrically, $S^{\circ}_{298} = 45.77$ eu.

Such calculations lead us to the conclusion that in many cases the thermodynamic functions determined by means of statistical methods on the basis of molecular characteristics are more accurate than those found by calorimetric measurements. At high temperatures encountered, for example, in plasma jets, the statistical methods are the only ones possible. True, under these conditions the approximation stipulated by relation (6.131) is no longer applicable, and one has to resort to the use of the method of direct summation or of more refined approximation methods.

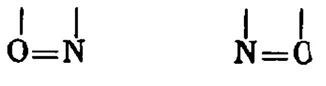
In concluding this section, let us consider the following example in connection with the above-given calculations and with the interpretation of the entropy as a measure of the disorder of the molecular state. The entropy of carbon monoxide as calculated by the statistical method is equal to 47.20 cal/deg·mole at 298.15°K. It has, however, been found by Clayton and Giauque by means of calorimetric measurements that the entropy of solid carbon monoxide at 0°K is only 46.2 cal/deg·mole lower than its entropy at 298.15°K. Thus, at absolute zero the entropy of solid carbon monoxide is not equal to zero and is 1.0 cal/deg·mole. This is evidently associated with the practical equivalence of the orientations of the carbon monoxide molecule (CO and OC in the crystal) and the resulting degeneracy equal to 2. If the ends of the CO molecules were oriented quite randomly, i.e., in approximately the following manner:



there would appear two possibilities of orientation (degeneracy) for each molecule or 2^{N_A} for N_A molecules in the crystal. Hence, the entropy corresponding to such disorder

$$S = \mathrm{k} \ln W = \mathrm{k} \ln 2^{N_A} = R \ln 2 \approx 1.4 \text{ cal/deg·mole}$$

In fact, the entropy at $T = 0$ is somewhat lower, which points to partially ordered orientations. An analogous picture obtains for the zero entropy of nitrous oxide, N_2O, and of long-chain olefins. For short-chain olefins there is probably a complete order. A situation similar to that with CO is observed in the case of NO. In the solid state, as we know, the structural unit of the crystal is the dimer N_2O_2. The N_2O_2 molecule is rectangular and is supposed to contain pairs of identical atoms at the corners along the diagonal. Therefore, two equivalent orientations of these molecules are possible in the crystal:



The observed residual (i.e., at $T = 0$) entropy, which is equal to 1.5 cal/deg·mole for the solid nitrogen oxide, is close to $R \ln 2$, which corresponds to the model indicated above.

6.19. Some Methods of Determination of Energy Levels and Other Molecular Characteristics[*]

In calculating the molecular partition function one must know the energy levels of a molecule and some other characteristics. These data can be found by studying the following optical spectra:

1. Emission spectra, i.e., spectra that arise when the molecule of a substance is excited, for example, by means of an electrical discharge.
2. Absorption spectra, especially in the infrared region (IR spectra).
3. Raman spectra.

TABLE 6.3. **Correction Factors for Some Energy Units Used in Spectroscopy and Chemistry**

	To convert →		Multiply by
	from	to	
6.947×10^{-14}	ergs/molecule	kcal/mole	1.439×10^{13}
4.336×10^{-2}	$\frac{\text{electron-volt}}{\text{molecule}}$	kcal/mole	23.061
3.498×10^{2}	$\frac{\text{cm}^{-1}}{\text{molecule}}$	kcal/mole	2.859×10^{-3}
5.034×10^{15}	$\frac{\text{cm}^{-1}}{\text{molecule}}$	ergs/molecule	1.986×10^{-16}
2.390×10^{-4}	kcal/mole	J/mole	4.1840×10^{3}
Multiply by	to	from	
	← To convert		

Electromagnetic radiation is known to be characterized by the frequency ν, i.e., the number of vibrations per second (s^{-1}), the wavelength $\lambda = c/\nu$ [cm], where c is the light velocity in a vacuum, equal to about 3×10^{10} cm/s, and also by the wavenumber[**], which is equal to the number of waves lying within 1 cm: $\omega = 1/\lambda$ [cm^{-1}].

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[*] For a more detailed treatment of the material dealt with in this section the reader is referred to the literature used by the author of this book: G. Herzberg, *Molecular Spectra and Molecular Structure*, 2nd ed., Van Nostrand Company, Inc., Princeton, N. J., 1950 and M. A. Elyashevich, *Atomic and Molecular Spectroscopy*, Fizmatgiz, Moscow, 1962 (in Russian).

[**] The wavenumber is also occasionally called the frequency and is designated as ν, though the two quantities are essentially different.

The frequency ν and the wavenumber ω are proportional to the radiation quantum energy and are therefore used (especially convenient is the wavenumber) for defining not only the quantum energy but also the energy level of a molecule. Table 6.3 presents correction factors for some widely used energy units.

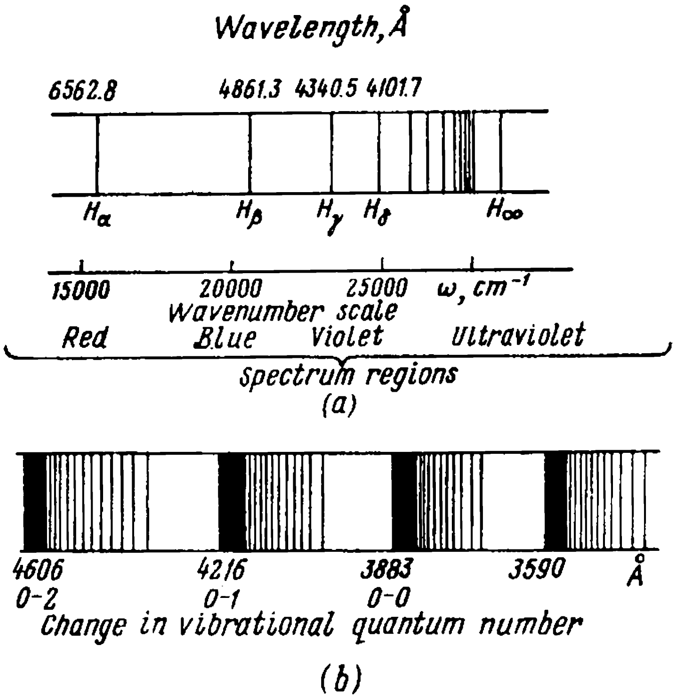

Fig. 6.19. Emission spectra in the visible and near ultraviolet regions (negatives): *a*—line spectrum of a hydrogen atom (the Balmer series): H_∞ indicates the boundary of the series, each line corresponding to an electron transition (Fig. 6.20*a*); *b*—the band spectrum of CN (the carbon arc in air); the system of bands corresponds to one electron transition, but from and to different vibrational and rotational levels. The band 00 is the transition from the zero vibrational level of the excited electronic state to the zero vibrational level of the ground state (according to Herzberg).

When an electrical discharge is passed through a rarefied monatomic gas (inert gases, metal vapours) there is observed a radiation whose spectrum consists of separate lines. A line spectrum is also observed in a gas composed of diatomic molecules but only in those cases when the molecules dissociate readily into atoms in a discharge. These include, for instance, hydrogen molecules which decompose under the action of electrons:

$$H_2 + \overleftarrow{e} \rightarrow H + H + \overleftarrow{e}$$

Figure 6.19*a* shows the spectrum of atomic hydrogen whose lines lie in the visible and near ultraviolet regions—this is the so-called *Balmer series**.

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* The H_α, H_β, H_γ and H_δ lines were originally measured by Fraunhofer as the absorption lines of the solar spectrum. Fraunhofer assigned the letters *C*, *F*, *f*, *h*, to these lines, respectively.

The emission spectra of diatomic molecules, to say nothing of polyatomic molecules, are considerably more complex. They consist of bands composed of very closely spaced lines. The distances between these lines are different—on one end they form a so-called edge if the resolution is not too strong. A band may be coloured either red or violet. Figure 6.19*b* shows the band spectrum of the CN molecule which arises upon burning a carbon arc in air.

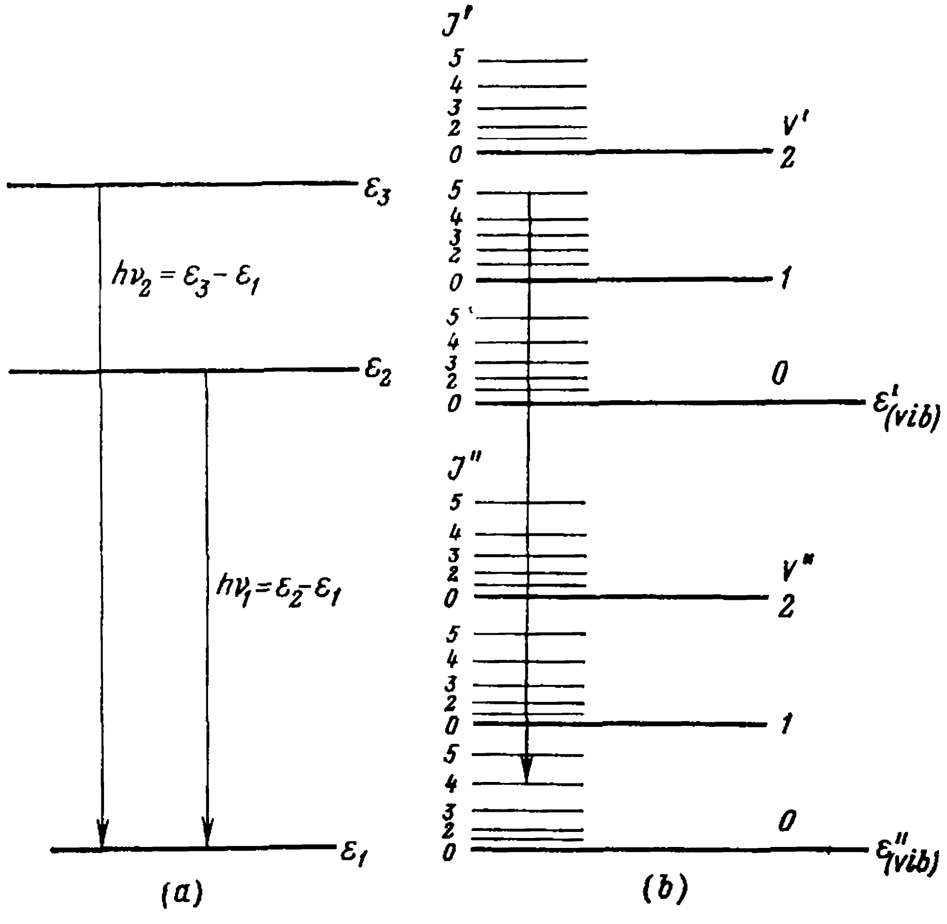

Fig. 6.20. Diagram of electronic energy levels in an atom (a line spectrum) (*a*) and diagram of vibrational and rotational energy levels of a diatomic molecule (*b*):

The arrow indicates the transition leading to the appearance of one line in the emission spectrum.

The above phenomena are explained by means of quantum mechanics. Emission appears when a molecule passes from a state of higher energy to a lower-energy state. In such a transition a quantum of electromagnetic radiation is emitted, its frequency being determined by the Bohr frequency rule:

$$h\nu = \varepsilon_2 - \varepsilon_1 \tag{6.196}$$

where ν is the radiation frequency; h is Planck's constant equal to 6.6252×10^{-27} erg·s (the quantum of action). The formation of a line spectrum is associated with changes in the electronic state of

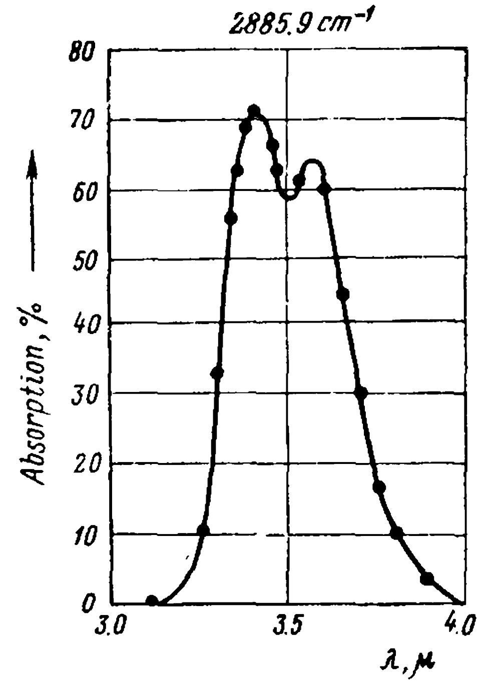

Fig. 6.21. The principal absorption band of HCl in the near infrared region (the Bjerrum doublet).

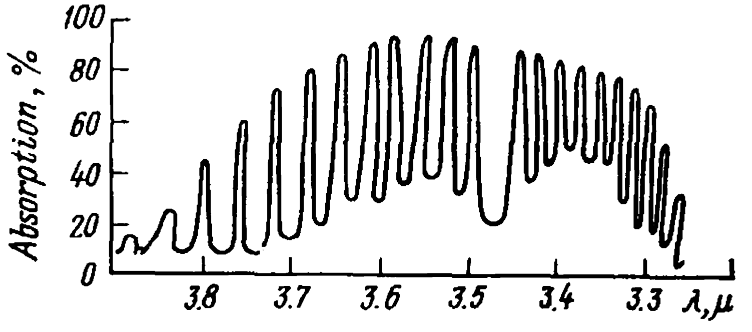

Fig. 6.22. The fine structure of the principal absorption band of HCl in the near infrared region.

monatomic molecules—with the transition of an electron to a lower-energy level. Figure 6.20*a* shows the disposition of three of the possible energy levels of an electron. The number of such levels is relatively small and they are, as a rule, separated by considerable energy intervals. Because of this, the number of possible transitions is not large and the spectrum lies in the visible and ultraviolet regions. In order to account for the formation of molecular band spectra it will be useful to cite some data on absorption spectra in the near ($\lambda < 20\mu$) and far ($\lambda > 20\mu$) infrared regions. It is exactly in the near infrared region that *absorption bands* are observed* for some molecules, say HCl, HBr, HI, CO, NO. One principal band with strong absorption predominates; there are also other bands, which are much weaker. When a low-resolution instrument is used, the band of HCl has the shape shown in Fig. 6.21, i.e., it consists of two closely spaced maxima (the Bjerrum doublet). The average wavelength at the absorption maximum is about 3.5 microns (μ). With the aid of a high-resolution spectrograph one can find that such a band consists of a series of lines (Fig. 6.22). In other words, the fine structure of an infrared absorption band is close to the structure of bands observed in the emission spectrum (see Fig. 6.19*b*) in the visible and ultraviolet regions. In the far infrared region ($\lambda > 20\mu$), for HCl and other hydrogen halides, for example, the absorption spectrum has a simple structure—several absorption maxima spaced at nearly equal distances from one another (Fig. 6.23). The ordinate in this figure represents the percentage energy transmission and therefore the minima of the curve correspond to the absorption maxima. The wavenumbers of the minima, i.e., the absorption lines, are expressed by a simple empirical formula: $\omega = f_0 m$ [cm^{-1}], where f_0 is a constant characteristic of a given gas; m is an integer. For HCl, $f_0 = 20.68$ cm^{-1}, and the observed lines have values of m ranging from 4 to 11.

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* Mainly with the aid of sensitive thermocouples.

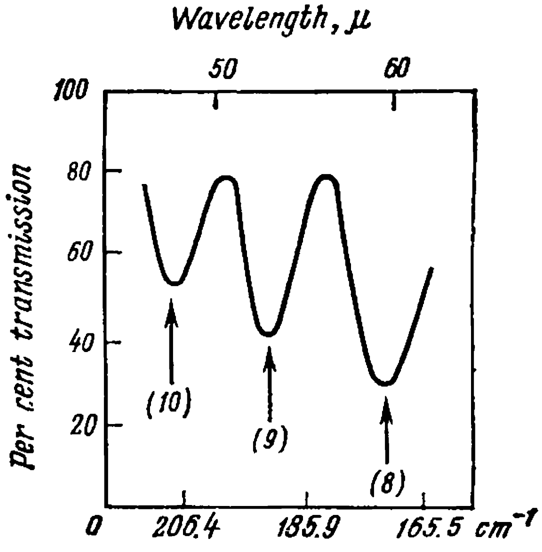

Fig. 6.23. The portion of the absorption spectrum of HCl in the far infrared region:

Given in parenthesis are the values of m in the empirical formula: $\omega_0 = f_0 m$; $f_0 = 20.68$ cm^{-1}; it corresponds to the theoretical formula (6.204), $\omega = 2B\,(J+1)$.

The complex nature of the spectra of diatomic and polyatomic molecules are accounted for by the fact that not only the energy of electrons can change (just as is the case with monatomic molecules) but also the vibrational energy of the atoms and the rotational energy of the molecule. According to the laws of electrodynamics, intramolecular motion leads to emission (or absorption) of light if it involves a change in the electrical moment of the molecule (see page 309). Only this kind of motion is sensitive, for example, toward the action of an electromagnetic field, which is accompanied by the absorption of radiation. Likewise, only such motions, while generating a variable field, can emit electromagnetic energy. In molecules with a constant dipole moment (say the molecules of hydrogen halides) a change in the electrical moment occurs when the molecule undergoes rotation or vibration. Therefore, in such cases, there are formed pure rotational and vibrational-rotational spectra.

The earlier-described absorption spectrum of HCl (or other hydrogen halides) in the far infrared region is treated as being a rotational spectrum, i.e., as being associated with the change of the rotational state of the molecule. The simplest molecular model used in this case to account for the spectrum is called a rigid rotator. For a diatomic molecule such a rotator is represented as a rigid dumbbell with its axis of rotation passing through the centre of mass. In quantum mechanics, the rotational energy of the rotator is expressed, as we already know from formula (6.154), in the following manner:

$$\varepsilon_{\text{rot}} = \frac{h^2}{8\pi^2 I} J(J+1) \tag{6.197}$$

where

$$J = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2 \tag{6.198}$$

is the moment of inertia of the rotating system, and the rotational quantum number J may assume the values 0, 1, 2, 3, ... Thus, the rigid rotator has a series of discrete energy levels, which depend on the value of J. Figure 6.24*a* shows a diagram of such energy levels in order of increasing energy. Further in the text we shall use, just as is customary in spectroscopy, not energy values but the proportional quantities—the terms corresponding to different levels. Expressing, as usual, the term in wavenumbers, we obtain:

$$F(J) = \frac{\varepsilon_{\text{rot}}}{hc}\,[\text{cm}^{-1}] = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1) \tag{6.199}$$

where h is Planck's constant; c is the light velocity; B is called the rotational constant—it is constant for a given rotator.

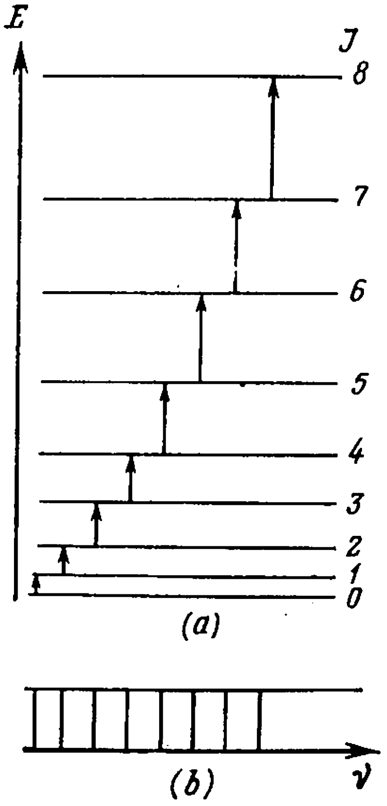

Fig. 6.24. Diagram of the energy levels of a rigid rotator:

a—transitions giving a spectrum in the far infrared region ($\lambda > 30\mu$); *b*—spectrum of a rigid rotator.

Radiation is emitted or absorbed when the molecule jumps from one energy level to another. The wavenumber of radiation is determined in accordance with the Bohr frequency rule (6.196) by the difference between the energies or terms:

$$\omega = F(J') - F(J'') = BJ'(J'+1) - BJ''(J''+1) \tag{6.200}$$

where J' and J'' refer, respectively, to states of higher and lower energy. An important selection rule has been established by means of methods of quantum mechanics: upon transition from one rotational level to another J can undergo a change only by ± 1. In other words, transitions are possible only between adjacent levels and

$$J' = J'' \pm 1 \quad \text{or} \quad \Delta J = J' - J'' = \pm 1 \tag{6.201}$$

Since we have agreed to assume that $J' > J''$, i.e., that J' refers to the upper state and J'' to the lower state, it will suffice to take into account that

$$J' = J'' + 1 \tag{6.202}$$

Substituting this value into Eq. (6.200) and dropping out the primes in J, we obtain a formula for the spectrum lines:

$$\omega = B\,(J + 1)\,(J + 2) - BJ\,(J + 1) \tag{6.203}$$

or

$$\omega = 2B\,(J + 1)\ \text{cm}^{-1}$$

where, as we know, $J = 0, 1, 2, 3, \ldots$.

Thus, the spectrum of the rigid rotator consists of a series of equidistant lines. The first absorption line with $\omega = 2B$ cm^{-1} will appear at $J = 0$, i.e., upon transition from the zero level to the first excited level of rotation $J' = 1$. The distance between the subsequent absorption lines is also 2 cm^{-1}. In Fig. 6.24*a* the arrows show transitions between the rotational levels upon absorption of radiation and Fig. 6.24*b* is a schematic representation of the absorption spectrum of the rigid rotator. In practice, there is observed an absorption picture of the type shown in Fig. 6.23. As has already been said, the minima of light transmission by a substance correspond in this figure to the absorption lines. By determining the distance between the minima we find $2B$. But since $B = h/8\pi^2 Ic$, then, if B is known, we can calculate I, i.e., from the spectrum in the far infrared region we determine an important molecular characteristic—its moment of inertia. The value of I and also the known atomic masses are used to calculate the internuclear distance r by means of formula (6.198). For example, for hydrogen chloride (see Fig. 6.23) $2B = f_0 = 20.68$ cm^{-1}, i.e., $B = 10.34$ cm^{-1}. Hence, the moment of inertia of the HCl molecule is $I = 2.71 \times 10^{-40}$ g·cm^2. But if we assume that the reduced mass $\mu = 1.63 \times 10^{-40}$ g, we will be able to find the internuclear distance, $r = 1.29 \times 10^{-8}$. This value of r is in satisfactory agreement with the values determined by other methods.

The absorption spectra in the near infrared region ($\lambda < 20\mu$) which contain the most intensive principal absorption band of the type shown in Fig. 6.21 for HCl are regarded as being due to a change in the mode of vibration in the molecule. Let us consider a molecular model known as the harmonic oscillator. As we already know from Sec. 6.17, only the following energy values are allowed for this kind of motion by quantum mechanics:

$$\varepsilon_{\text{vib}} = h\nu_{\text{vib}}\left(v + \frac{1}{2}\right) \tag{6.204}$$

where ν_{vib} is the vibrational frequency of the oscillator, s^{-1}; v is the vibrational quantum number which assumes the values $0, 1, 2, 3, \ldots$.

To convert from the energy to the terms, Eq. (6.204) should be divided by *hc*:

$$G_v = \frac{\varepsilon_{\text{vib}}}{hc} = \frac{\nu_{\text{vib}}}{c}\left(v+\frac{1}{2}\right) = \omega_{\text{vib}}\left(v+\frac{1}{2}\right) \qquad (6.205)$$

where ω_{vib} is the wavenumber of the vibrations of the oscillator, cm^{-1}. The absorption or emission of radiation again occurs in accordance with the Bohr frequency rule, when the vibrational state of the molecule undergoes a change. The wavenumber ω of such radiation will be equal to the difference between the terms of the corresponding vibrational levels:

$$\omega = G_{v'} - G_{v''} \qquad (6.206)$$

where, as before, v' refers to a state of higher energy and v'' to a state of lower energy. In this case too, quantum mechanics leads to a selection rule that shows that v, just like J for the rigid rotator, can change only by unity, i.e.

$$\Delta v = \pm 1$$

Therefore by combining Eqs. (6.206) and (6.205) at $v' = v'' + 1$, we obtain the wavenumber of the absorbed radiation, dropping out the primes:

$$\omega = \omega_{\text{vib}}\left(v+1+\frac{1}{2}\right) - \omega_{\text{vib}}\left(v+\frac{1}{2}\right) = \omega_{\text{vib}} \qquad (6.207)$$

or $\omega = \omega_{\text{vib}}$. Thus, it appears that the wavenumber of the radiation emitted or absorbed by the harmonic oscillator is equal to the wavenumber of the vibrations of the oscillator itself, which is a first-approximation model of the vibrating molecule. It is immaterial here which levels are combined—the zero level with the first level, the first level with the second, etc. We may resort here to Fig. 6.13, which shows the dependence of the energy of the harmonic oscillator on the internuclear distance (a parabola). The figure also shows the equidistant energy levels and transitions between them, which lead to the absorption or emission of radiation quanta of equal energy and, hence, of frequency.

As has been said above, the hydrogen chloride molecule has one intensive absorption band at $2885.9\ \text{cm}^{-1}$ in the near infrared region. According to the interpretation given, this will also be the wavenumber of atomic vibrations in the molecule. In other words, the frequency of such vibration in HCl is given by

$$\nu_{\text{vib}} = \omega c = 8.65 \times 10^{13}\ \text{s}^{-1} \qquad (6.208)$$

On the basis of the relation $\nu = \frac{1}{2}\pi\sqrt{K_e/\mu}$ we can find the force constant for HCl:

$$K_e = 4.8 \times 10^5\ \text{dynes/cm} \qquad (6.209)$$

To what has been said about the absorption spectrum in the near infrared region we should add the following. First, the selection rule $\Delta v = \pm 1$, which is strictly valid for the harmonic oscillator, may become invalid in the case of the anharmonic oscillator, which is a molecular model of a more accurate approximation. Therefore, not a single principal absorption band is actually observed but a series of considerably much less intensive bands (the second band is less intensive by about 10, the third by 100, the fourth by 1000 times).

Second, the appearance of a band of fine structure observed with the aid of a high-resolution instrument (see Fig. 6.22) is accounted for by the fact that the change in the vibrational energy associated with a change in v can be accompanied by a change in the rotational energy of the molecule which depends on J. Rotational transitions correspond to much lower energies than do vibrational transitions (the difference is by 10 or more times). One vibrational transition can be accompanied by various changes in the rotational state. It is this circumstance that leads to the formation of a band consisting of separate rotational lines. Thus, Figs. 6.21 and 6.22 show a so-called vibration-rotation spectrum, whereas the spectra shown in Figs. 6.23 and 6.24 are pure rotational spectra.

Third, as has already been mentioned, the interaction of a substance with infrared radiation which is accompanied by the absorption of radiation and also the emission of radiation in this region of the spectrum is possible for molecules in which the rotation and vibration are accompanied by a change in the electrical moment (the dipole moment). In molecules composed of identical atoms (O_2, N_2, H_2, etc.) the dipole moment is equal to zero and does not appear in the course of either vibrations or rotations; therefore, for such substances there is no emission or absorption in the infrared region. The changes of vibrational and rotational states can, however, be accompanied by electronic transitions and also occur when the light is scattered.

We have so far dealt with only the vibrational and rotational energies of molecules. The appearance of band spectra in the visible and ultraviolet regions, say the spectrum of CN shown in Fig. 6.19*b*, is associated, first of all, with a change in the electronic energy accompanied by a change in the vibrational and rotational energies. On the whole as has already been pointed out (Sec. 6.16), the intramolecular energy can be represented approximately* as the sum of the energies of electronic, vibrational and rotational motions: $\varepsilon = \varepsilon_{el} + \varepsilon_{vib} + \varepsilon_{rot}$. With the energy of a molecule being split into the components, the different orders of magnitude of the electronic, vibrational and rotational energies become very important. The electronic energy of a molecule is of the same order as in an atom. It is much higher than the vibrational energy, and the vibrational energy is much greater than the rotational energy: $\varepsilon_{el} \gg \gg \varepsilon_{vib} \gg \varepsilon_{rot}$.

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* That is, without taking into account the energy of interaction between the individual types of motions.

It may be assumed approximately that the above-indicated kinds of energy relate to one another in the following ratio: 100 : 10 : 1. We can therefore imagine the disposition of the energy levels of a molecule as similar to that shown in Fig. 6.19*b*. To one electronic level of the molecule there correspond many vibrational levels, and to each vibrational level there correspond many rotational levels.

Upon transition of the molecule from one state to another all the three components of the total energy of the molecule—the electronic, vibrational and rotational—may undergo a change. This will bring about the emission or absorption of a quantum of electromagnetic radiation. According to the Bohr frequency rule, we have

$$h\nu = \varepsilon' - \varepsilon'' = (\varepsilon'_{el} - \varepsilon''_{el}) + (\varepsilon'_{vib} - \varepsilon''_{vib}) - \\ - (\varepsilon'_{rot} - \varepsilon''_{rot}) = \Delta\varepsilon_{el} + \Delta\varepsilon_{vib} + \Delta\varepsilon_{rot} \qquad (6.210)$$

According to what has been said, $\Delta\varepsilon_{el} \gg \Delta\varepsilon_{vib} \gg \Delta\varepsilon_{rot}$. Transitions obey selection rules similar to those mentioned earlier, and, as a result, there appear band spectra of the type shown in Fig. 6.19*b*, which lie, as a rule, in the visible and ultraviolet regions. Such spectra should be called electronic-vibration-rotation spectra or, simply, electronic spectra. Thus, whereas an electronic transition in an atom gives rise to a single line in the spectrum, in a molecule for a single electronic transition there may be many lines grouped into bands.

If $\Delta\varepsilon_{el}$ in Eq. (6.210) is equal to zero, i.e., the mode of motion in the molecule is changed within a given electronic state, a vibration-rotation spectrum appears, which lies, as we already know, in the near infrared region. If $\Delta\varepsilon_{vib}$ is also equal to zero, the rotational spectrum described above will be formed in the far infrared region.

A study of electronic spectra can provide essential information on the energy levels of a molecule and, in the first place, on its electronic states and properties. A more detailed examination of electronic spectra and the associated important phenomena, say the appearance of a continuous spectrum, is beyond the scope of this book.

Let us now turn our attention to Raman spectra. If a substance (a gas, liquid, or crystal) is illuminated by a parallel beam of monochromatic light, i.e., light which gives only a single line in the spectrum*, then scattered light can be observed at a right angle to the transmitted light (Fig. 6.25). The spectrum of the scattered light will contain, first, an intense line of the incident light scattered without change in frequency—this is the so-called Rayleigh scattering. With sufficiently high exposures, when the parent line appears to have been strongly overexposed, ghost lines appear on the photograph—weak lines which were absent in the light source and which lie to the right and left of the parent line. This phenomenon was first detected in India by Raman and Crishna and, independently, by Mandelshtam and Landsberg in the USSR. It is called the *Raman effect* or *Raman scattering*.

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* We speak of a single line for the sake of simplicity. In practice, use is made of a light source with a well-defined line spectrum, say a mercury arc lamp, and the Raman spectrum of any line (say, the line at 2537.5 Å) is studied.

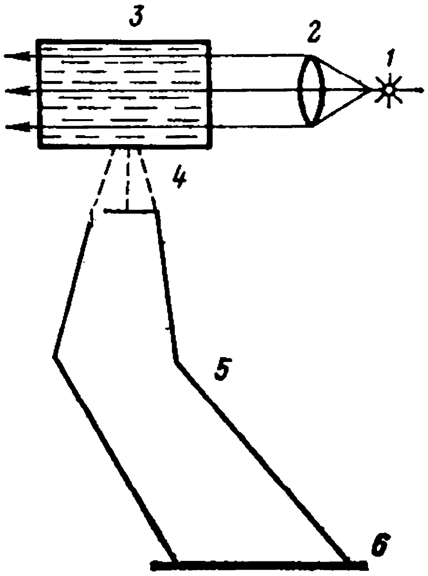

Fig. 6.25. Observation of the Raman spectrum:

1—source of monochromatic light; 2—lens; 3—sample cell; 4—scattered light; 5—spectrograph; 6—photographic plate holder.

The shift of the Raman line relative to the line of the incident light is independent of the position of this line in the spectrum (i.e., of its frequency or wavenumber) and is a characteristic of the substance that scatters radiation.

It is most convenient to study spectra of this type in the visible and ultraviolet regions, using the method of photographic recording. The shifts may be classified into large and small. Under moderate resolution a diatomic gas displays a single relatively intense line shifted toward longer wavelengths and weak lines situated between the shifted line and the principal line. As has been found, large shifts coincide with the wavenumbers of the absorption lines in the

TABLE 6.4. **Large Raman Shifts and Infrared Frequencies of Diatomic Gases (according to G. Herzberg)**

Gas	Raman shift, cm^{-1}	Absorption frequency in the near infrared, cm^{-1}
HCl	2886.0	2885.9
HBr	2558	2559.3
HI	2333	2330.1
NO	1877	1879
CO	2145	2144
H_2	4160.2	Absent
N_2	2330.7	Absent
O_2	1554.7	Absent

near infrared, i.e., with the vibrational frequencies of atoms in a molecule [formula (6.207), Table 6.4]. Thus, a study of Raman spectra in the visible region can replace a more difficult examination of spectra in the invisible infrared region. It is also important that Raman spectra are displayed by homonuclear molecules, such as H_2, N_2, O_2, which do not exhibit infrared absorption since their intramolecular motions are not associated with change in the dipole moment.

With a high-resolution spectrograph, in addition to the above-indicated line which becomes broader, approaching a band, a series of equidistant lines appear on both sides of the Rayleigh line (Fig. 6.26). The spacing between these lines is

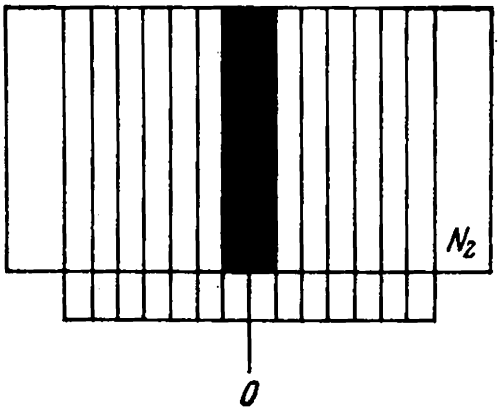

Fig. 6.26. The rotational Raman spectrum of the nitrogen molecule:
0 -Rayleigh scattering line (after Razetti).

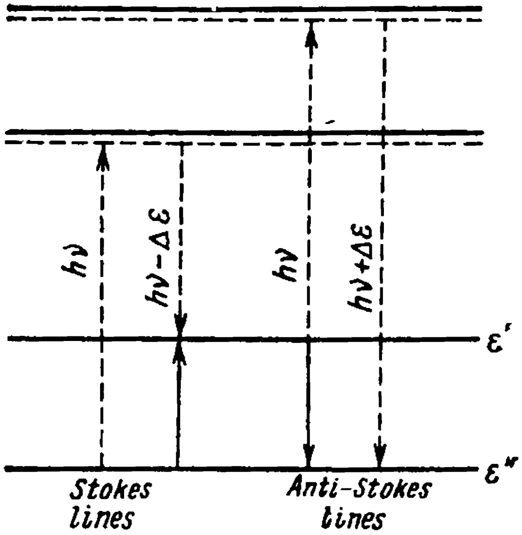

Fig. 6.27. A quantum-mechanical interpretation of the origination of Raman spectra:
ε'' and ε' are two energy levels of the molecule; the upper broken lines do not correspond to any level; they only denote the energy $h\nu$ of transmitted light.

$$l \approx 2f_0 \simeq 4B \tag{6.211}$$

where B is the rotational constant of the molecule. Therefore, the appearance of this spectrum of small shifts is associated with the rotational characteristic of molecules. Thus, the observation of small shifts is a method of determination of the constant B and, hence, of the moment of inertia and the internuclear distance of the molecule.

Quantum theory provides the following explanation for Raman spectra. A light quantum when colliding with a molecule can experience elastic and inelastic collisions. In elastic collisions the quantum energy $h\nu$ does not change; only the direction of its motion is changed—this is Rayleigh scattering. In inelastic collisions a quantum can give part of its energy to a molecule, as a result of which the molecule is transferred from the level ε'' to the level ε' (Fig. 6.27).

The scattered quantum will have a lower energy, namely, $h\nu - \Delta\varepsilon$, where $\Delta\varepsilon = \varepsilon' - \varepsilon''$. In the spectrum there will appear a line with a small wavenumber as compared with the wavenumber of the incident light. Such lines are called *Stokes lines.*

In another case, a quantum of the incident radiation can collide with a molecule which is already at the level ε', i.e., in the excited state. In the process of interaction between the particles, i.e., the quantum and the molecule, the latter can return to the state ε'', in which case the scattered quantum will have a higher energy: $h\nu + \Delta\varepsilon$, and in the spectrum there will appear a line (known as an *anti-Stokes line*) with a wavenumber greater than that of the incident light. Large shifts equal to absorption frequencies in the near infrared region probably correspond to the energy levels of the zero (ε_0) and first (ε') vibrational states. Since, according to Fig. 6.14, the vibrational levels at low temperatures are excited little, diatomic molecules do not practically display anti-Stokes lines. Small shifts in the form of the equidistant lines indicated above are associated with the change of the rotational states, which are excited (Fig. 6.15) even at room temperature, and therefore the appearance of anti-Stokes lines is probable (Fig. 6.27). The two-fold difference in the spacing between rotational lines in Raman and infrared spectra is accounted for by a different selection rule for the rotator*: $\Delta J = 0, \pm 2$ instead of $\Delta J = \pm 1$, both for the generation and absorption of infrared radiation.

According to theoretical investigations, Raman scattering is associated with the appearance of an induced dipole moment in scattering molecules and, hence, with their polarizability. The latter is defined by the relation

$$\mu_{\text{ind}} = \alpha E \tag{6.212}$$

where E is the electric field strength; μ_{ind} is the electric moment induced under the influence of the field; α is the proportionality factor called the polarizability. The quantity α is usually expressed in cm^3 since it has the dimensions of volume. The order of magnitude of the polarizability is 10^{-24} cm^3. In the case of light scattering the induced moment is created under the influence of the electric field of the incident electromagnetic wave. This field varies periodically by the cosine law:

$$E = E_0 \cos 2\pi\nu_0 t \tag{6.213}$$

where E_0 is the amplitude; ν_0 is the variation frequency, s^{-1}. When a molecule interacts with the wave field, an induced dipole moment appears, which varies with the field frequency ν_0. In other words, a varying electric dipole is produced, which itself emits energy in all directions. Such is the classical picture of light scattering. If the polarizability α in Eq. (6.212) is constant, i.e., is equal to α_0, then the frequency of the light being scattered coincides with ν_0 (Rayleigh scattering). For a real molecule, however, the polarizability itself changes with the vibrational frequency of the molecule, ν_{vib}, i.e.,

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* For the harmonic oscillator the selection rule $\Delta v \pm 1$ remains to be valid.

$$\alpha = \alpha_0 + \alpha_\nu \cos 2\pi\nu_{\text{vib}}t \tag{6.214}$$

In such a case, Raman scattering takes place. By combining formulas (6.212), (6.213) and (6.214) and using simple trigonometric transformations, it is not difficult to show that the total induced moment μ_{ind} will contain, in addition to the term μ_{ν_0} which changes with frequency ν_0 and is the cause of Rayleigh scattering, also the terms $\mu_{\nu_0-\nu_{\text{vib}}}$ and $\mu_{\nu_0+\nu_{\text{vib}}}$ which change with frequencies $\nu_0 - \nu_{\text{vib}}$ and $\nu_0+\nu_{\text{vib}}$, respectively. These components are responsible for Raman scattering, i.e., a Stokes line with frequency $\nu' = \nu_0 - \nu_{\text{vib}}$ and shift* $\nu_{\text{vib}} = \nu_0 - \nu'$ $(\nu_0 > \nu')$, and also an anti-Stokes line with frequency $\nu'' = \nu_0 + \nu_{\text{vib}}$ and shift toward short wavelengths $\nu_{\text{vib}} = \nu_0 - \nu''$ $(\nu_0 < \nu'')$. Both shifts are equal to the natural vibration frequency of the molecule.

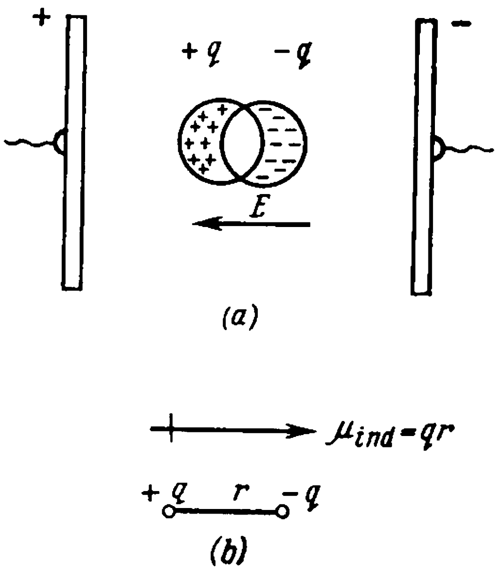

Fig. 6.28. Appearance of the induced dipole moment:

a—drifts of molecular charges in a capacitor with the field intensity E, V/cm; b—representation of extra charges in the form of point charges q separated by the distance r (shown above is the direction of the dipole moment).

From the foregoing it follows that the formation of infrared and Raman spectra is connected with the electrical properties of the molecule—the electric dipole moment and polarizability. It is therefore appropriate to dwell here in more detail on these properties, the more so that the determination of the permanent dipole moment can contribute to the elucidation of the geometric configuration of the molecule. The molecular polarizability α defined by relation (6.212) characterizes, as it were, the deformability of the molecule under the action of an external electric field E. Under the influence of the field the electrical charges in the molecule are shifted, so that, on one hand, there is formed an excess of positive charge $(+q)$ and, on the other, an excess of negative charge $(-q)$ (Fig. 6.28a). In what follows excess charges may be regarded as being concentrated in their "centres of mass", i.e., as point charges $+q$ and $-q$ separated by a distance r (Fig. 6.28*b*). Then the induced dipole moment that appears will be defined by the relation $\mu_{\text{ind}} = qr = \alpha E$. Here use is made of expression (6.212) which relates μ_{ind} to the field strength.

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* As mentioned earlier, a "large shift".

Without delving into the details, we shall point out that the molecular polarizability governs the dielectric properties of a substance which are characterized by its dielectric constant D. The dielectric constant D is a quantity measured directly by experiment. More exactly, as known, one actually measures the capacity of a parallel-plate capacitor C with a given substance as a dielectric and the capacity C_0 for vacuum:

$$D = \frac{C}{C_0} \tag{6.215}$$

An important quantity is the *molar polarization* defined as

$$P_D = \frac{4}{3}\pi N_A \alpha \tag{6.216}$$

that is, a measure of the total electric dipole moment in one mole of substance at the field strength $E = 1$ V/cm, which results from the deformation of the molecule.

The Clausius-Mosotti equation connects the molar polarization with the dielectric constant:

$$P_D = \frac{4}{3}\pi N_A \alpha = \frac{D-1}{D+2}\frac{M}{d} \simeq 2.54 \times 10^{24}\alpha \tag{6.217}$$

where M is the molar mass; d is the density of the substance. Thus, having measured D, we can find an important property of the molecule—its polarizability.

The Clausius-Mosotti equation does not reflect the dependence of molar polarization on temperature. As a matter of fact, there are many substances for which the molar polarization is independent of temperature. Examples among gases are H_2, N_2 and O_2, all hydrocarbons of symmetrical structure: methane, ethylene, acetylene, benzene, etc. For many substances, however, the molar polarization* does depend on temperature. For example, for ammonia $P = 57.57$ cm³/mole at $T = 292.2$°K; at $T = 466.0$°K the polarization falls down to 39.59 cm³/mole. The second category of substances are characterized exactly by a decrease in molar polarization with increasing temperature. Debye ascribed this fact to the presence in such molecules of a dipole moment even in the absence of an external electric field. The formation of such a permanent dipole moment is accounted for by the natural asymmetry of the molecule. When a substance consisting of polar molecules is placed in an electric field, the polarization that appears is associated with two factors:

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* For the molar polarization of such substances we use the symbol P, in distinction to the deformation polarization P_D which is independent of temperature.

1. Polarization due to the action of the field that causes a change in the dipole moment. This is *deformation polarization*; as before, it depends on the polarizability and is equal to $(4\pi N_A/3)\alpha$.

2. *Orientational polarization.* The permanent molecular dipoles tend to orient their vectors (see Fig. 6.28) parallel to the field strength vector. This orientation increases the total polarization of the substance since it leads to addition of the dipole moments.

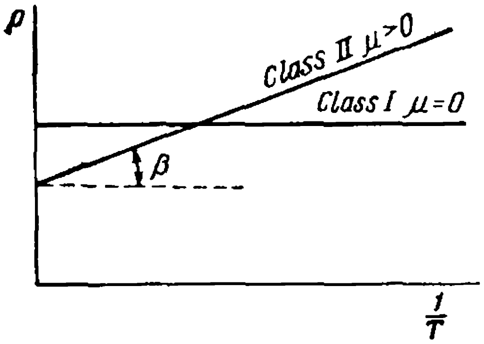

Fig. 6.29. The molar polarization P versus the inverse temperature for two classes of substances.

According to Debye, the effect of temperature consists in this orientation being distorted by thermal motion. As the temperature is raised, i.e., as the thermal motion of molecules becomes more intensive, the total molar polarization must decrease. For substances with a permanent dipole moment the Clausius-Mosotti equation is replaced by the Debye formula:

$$P=\frac{D-1}{D+2}\,\frac{M}{d}=\frac{4}{3}\,\pi N_A\alpha+\frac{4}{3}\,\pi N_A\,\frac{\mu^2}{3kT} \qquad (6.218)$$

where μ is the permanent dipole moment of the molecule.

The Debye formula holds for gases and vapours of medium density; it can also be applied to dilute solutions of polar substances in nonpolar solvents (for example, CCl_4). Permanent dipole moments are determined experimentally by studying the dependence of P on temperature in accordance with Eq. (6.218). This dependence can be given in the form:

$$P=f(T)=a+b\,\frac{1}{T} \qquad (6.219)$$

where

$$a=\frac{4}{3}\,\pi N_A\alpha \quad \text{and} \quad b=\frac{4}{3}\,\pi N_A\,\frac{\mu^2}{3kT}$$

According to what has been said above and also formula (6.219), all substances can be divided into two classes in accordance with the character of the temperature dependence of polarization P (Fig. 6.29). Typical of class I is a horizontal line which shows that P is independent of T. Here $\mu = 0$. The line for class II has a slope equal to $\tan\beta = b = 4/3\pi N_A\,(\mu^2/3kT) = 3.16 \times 10^{-7}\,\mu^2$, i.e., the slope is proportional to the square of the dipole moment. Thus, the determination of the permanent dipole moments of molecules is based on measurements of the dielectric constants of substances at various temperature, including sufficiently high temperatures. This is not an easy experimental task.

An idea of the order of magnitude of dipole moments and their units of measurement can be obtained in the following way. The distance between the centres of mass of charges is of the order of magnitude of molecular dimensions, i.e., 10^{-8} cm, and the charges are of the order of magnitude of the electronic charge equal to 4.802×10^{-10} absolute units. Dipole moments are measured in Debye units; assuming that $\mu = 10^{-18}$ e.s.u. = 1 Debye = 1 D.

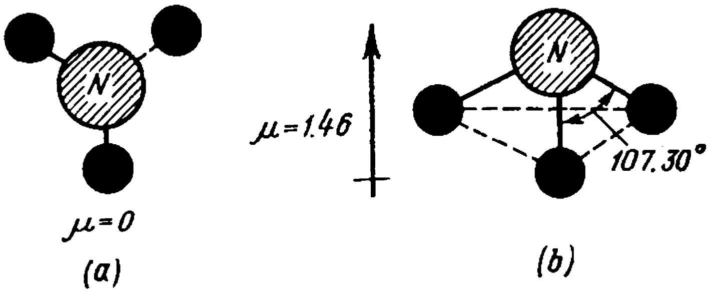

Fig. 6.30. Conceivable models of the ammona molecule:
a—two-dimensional symmetric model is incompatible with the presence of an observed dipole moment; b—pyramidal asymmetric model corresponds to the observed moment μ = 1.48 D.

It is clear that the factor responsible for a permanent dipole moment in molecules is their asymmetry, which determines the non-coincidence of the centres of mass of the charges. Therefore, based on the absence or presence of a dipole moment and also on its absolute magnitude we can get an idea of the nature of the symmetry (or asymmetry) of a molecule and draw certain conclusions as to the geometric arrangement of its atoms. Let us consider some examples.*

For ammonia, NH_3, several structures can be suggested *a priori*. For example, a planar symmetrical configuration (Fig. 6.30*a*), but such a configuration is not expected to have a dipole moment and ammonia does possess a dipole moment (μ = 1.46 D). To the presence and magnitude of μ there corresponds the widely adopted pyramidal structure with the angle between the N—H bonds equal to 107.3° (Fig. 6.30*b*). The high dipole moment of the water molecule (μ = 1.84) points to the nonlinear arrangement of the hydrogen and oxygen atoms (Fig. 6.31). The same could be said about the triatomic molecules SO_2 and H_2S—their atoms form an isosceles triangle.

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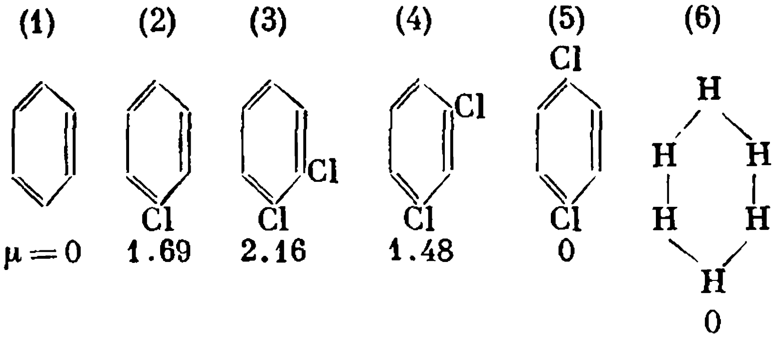
* All the dipole moments given are taken from *Chemist's Handbook*, vol. I., Goskhimizdat, Moscow, 1963, pp. 963-966 (in Russian).

On the other hand, the CO_2 and CS_2 molecules are nonpolar and are therefore linear (Fig. 6.32). Very characteristic is the change of μ in the series of benzene and its derivatives:



The largest value of dipole moment corresponds to the least symmetrical configuration of *ortho*-dichlorobenzene (3). For symmetrical molecules—benzene (1), *para*-dichlorobenzene (5) and cyclohexane (6) the dipole moment $\mu = 0$.

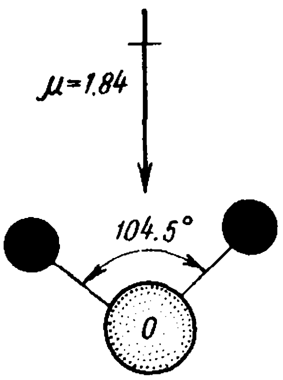


Fig. 6.31. The non-linear model of the water molecule.

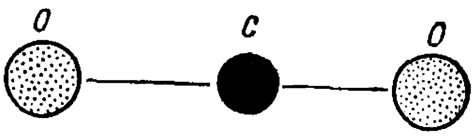


Fig. 6.32. The linear structure of the CO_2 (or CS_2) molecule.

Thus, among other data, a study of the electrical properties of molecules makes it possible, in a number of cases, to approach the elucidation of their structure, for example, by way of a choice of alternative structures. As regards other sources of information on the molecular structure, apart from the methods described in this section, gas electron diffraction studies, electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) have found wide application.

Chapter 7

Solutions

7.1. General Remarks and Concentration Units

Solutions are defined as homogeneous systems consisting of two or more substances (components), whose composition may vary continuously within certain limits. Thus, solutions differ from chemical compounds in that their composition is not constant and they do not obey the law of multiple proportions.

Solutions may exist in any of the three states of aggregation: there are solid, liquid and even gaseous solutions, the latter meaning gas mixtures. Gaseous mixtures (more exactly, ideal gas mixtures) have been considered to a certain extent in Chapter 5 in connection with chemical equilibrium. Solid solutions, which constitute the subject matter of solid-state physics and physical métallurgy, will be treated in more detail in Chapter 8. In this chapter we shall be concerned only with liquid solutions, systems which vary widely in their nature and intermolecular interaction. For instance, when sulphuric acid is dissolved in water, a large amount of heat is evolved and a series of *hydrates* of definite composition are formed. Partly on the basis of these observations Mendeleev developed his chemical theory of solutions. Undoubtedly, the forces that act in the above-mentioned hydrates of sulphuric acid are similar by their nature to the forces of chemical bonds. As another extreme case we can mention solutions of substances, such as argon and neon (or other elements of Group Zero), where only forces of physical nature are operating—relatively weak van der Waals forces.

The general task of the theory of solutions must consist of the determination of the properties of solutions on the basis of the properties of their components. It must be said that this principal task is at present far from being solved in a more or less general form. More success has been achieved in establishing regularities that provide relations between the properties. One of the main properties of solutions is the concentration, which is determined in terms of various units. We shall give these units of concentration measurement in addition to what has been said in Chapter 1, dividing them into two categories. In the first category, the amount of substances that compose a solution is referred to a known amount of solution.

1. The *weight fraction* is given by

$$w_i = \frac{g_i}{\sum g_j} \tag{7.1}$$

where g_i is the weight of a component of the solution; 100 w_i represents the weight percent of the component in the solution.

2. The *mole fraction*

$$N_i = x_i = \frac{n_i}{\sum n_j} \tag{7.2}$$

where n_j is the number of moles of components; 100 N_i will express the mole per cent.

3. The *volume fraction* is written in the form of the ratio

$$\varphi_i = \frac{v_i}{V} \tag{7.3}$$

of the volume of the component, v_i, to the volume of the solution, V. Likewise, $100\varphi_i$ will be the per cent by volume, which coincides with the mole per cent for ideal gas mixtures (just as the corresponding fractions). Obviously, the value of any of the fractions may vary only within the limits from zero to unity.

4. An important concentration unit is the *molarity*, which is often called simply the *concentration* and defined as the ratio of the number of moles of solute to the volume of solution:

$$c_i = \frac{n_i}{V} \tag{7.4}$$

The molarity is widely used in chemical kinetics since the rate of a reaction is determined exactly by values of c_i. A version of this unit, the normality of a solution, is used in analytical chemistry.

In the second category, the amount of solute is referred to a definite amount of solvent.

1. The *mole ratio* is defined as

$$r_i = \frac{n_i}{n_1} \tag{7.5}$$

that is, as the ratio of the number of moles of solute per 1 mole of solvent.

2. The *molality* of a solution has some advantages. It is defined as

$$m_i = \frac{n_i 1000}{g_1} = \frac{n_i 1000}{n_1 M_1} \tag{7.6}$$

which expresses the number of moles of solute per kilogram of solvent. Unlike the widely used molarity (c_i), the molality is independent of temperature.

There are certain relations between the concentration units, which are used, if necessary, to convert from one concentration unit to another. We shall only note that for dilute solutions all the concentration units are proportional to each other.

7.2. Partial Molar Quantities

In this section we shall once more be concerned with the concept of partial molar quantities, an important concept in the thermodynamics of solutions. We have already partly considered these quantities in Chapter 1 while discussing the extensive properties of a system and also in Chapter 5 in connection with the chemical potential, which is also known as the partial molar Gibbs free energy. Let us consider this quantity in detail. We shall refer to the volume of solution. Is it equal to the sum of the volumes of the components? Generally speaking, it is not. For example, when ethyl alcohol (ethanol) is mixed with water, the total volume is decreased. The volume of a solution may be either smaller or larger than the sum of the volumes of the components taken separately. Nevertheless, each of the components makes its own contribution to the volume or any other extensive property of the solution (for example, the energy). It is for the estimation of this contribution that the partial molar quantities are used.

Let a binary solution contain n_1 moles of substance A_1 (solvent) and n_2 moles of substance A_2. The total volume of the solution is denoted as V. We add a small amount, dn_2, of the second substance—the volume of the solution will be changed by dV. The ratio

$$\left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1}=\bar{v}_2 \tag{7.7}$$

will exactly define the partial molar volume of the second substance in the solution of given composition. In other words, $\bar{v}_2$ is the change in the total volume of the solution per 1 mole of substance added in a small amount. In contrast to the molar volume of a pure substance (designated as $\underline{v}$), the partial molar volume may be either positive or negative. For instance, the addition of the salt $MgSO_4$ to a dilute solution brings about a decrease in the volume. Therefore. in this particular case

$$\bar{v}_2=\left(\frac{\partial V}{\partial n_2}\right)_{p,T,n_1}<0 \tag{7.8}$$

that is, the partial molar volume of magnesium sulphate in this solution is negative.

Let us now consider methods of determining partial molar quantities. First, we shall describe the graphical method which is especially suitable for substances miscible in any proportions (like alcohol and water). In such cases, when studying binary (two-component) solutions, use is made of special graphs: the mole fractions of both components are laid off along the abscissa and the properties of the pure components along the two ordinates, and the intermediate values of the ordinates express the property of the solution being studied. We are now concerned with the volume of solution. Let us define the molar volume of the solution by means of the relation

$$\underline{v}=\frac{V}{n_1+n_2} \qquad (7.9)$$

and plot the dependence $\underline{v}=f(N_1, N_2)$ on the basis of experimental data (Fig. 7.1). The convex curve shows that the volume of the solution, $\underline{v}$ is not additively made up of the volumes of the pure components, $\underline{v}_{01}$ and $\underline{v}_{02}$. In order to find the partial volumes of the components of the solution of composition a one should draw a tangent to the curve $\underline{v}$ at point a' and find the intercepts $\overline{AB}$ and $\overline{A'B'}$ cut off by the tangent on the ordinates. The partial molar volumes are then equal to

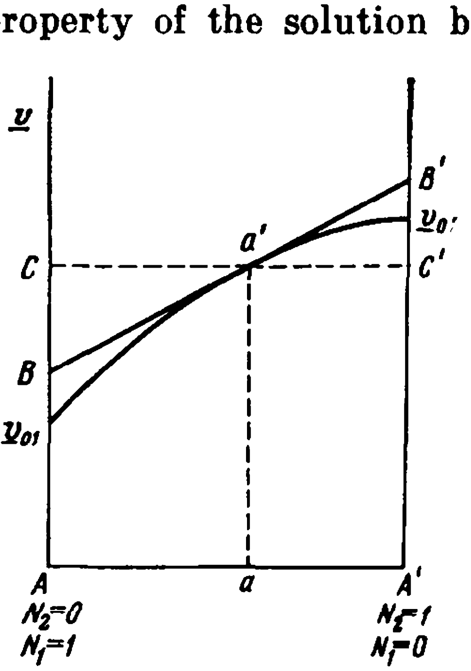


Fig. 7.1. Determining the partial molar volume of a component of a solution.

$$\bar{v}_1=\overline{AB} \text{ and } \bar{v}_2=\overline{A'B'} \qquad (7.10)$$

Let us prove these equalities (the rule of intercepts). If the first of relations (7.10) is valid, then we can write on the basis of the graph in Fig. 7.1:

$$\bar{v}_1=AB=\overline{AC}-\overline{BC} \qquad (7.11)$$

but $\overline{AC}=\underline{v}$, i.e., the molar volume of solution of composition a. On the other hand, when examining the triangle $Ba'C$, we see that $\overline{BC}=N_2\,(d\underline{v}/dN_2)$. Thus, relation (7.11) becomes

$$\bar{v}_1=\underline{v}-N_2\frac{d\underline{v}}{dN_2} \qquad (7.12)$$

and if we prove it, we shall thereby prove the rule of intercepts.

Proceeding from the relations

$$\underline{v}=\frac{V}{n_1+n_2} \text{ and } N_2=\frac{n_2}{n_1+n_2} \qquad (7.13)$$

we must remember that we are concerned here with molar quantities and that the amounts of solutions are immaterial. Therefore, let us agree on preparing a solution by adding any required amount of solvent A_1 to some definite constant amount of solute A_2. Stated another way, by varying the composition of the solution we assume that n_1 is variable and n_2 is constant. Differentiating relations (7.13) on this condition, we obtain:

$$d\underline{v}=\frac{dV}{n_1+n_2}+V\frac{dn_1}{(n_1+n_2)^2} \tag{7.14}$$

and

$$dN_2=-\frac{n_2}{(n_1+n_2)^2}dn_1 \tag{7.15}$$

Dividing Eq. (7.14) by Eq. (7.15) and cancelling, we get:

$$\frac{d\underline{v}}{dN_2}=-\frac{dV}{dn_1}\frac{n_1+n_2}{n_2}+\frac{V}{n_2} \tag{7.16}$$

We multiply Eq. (7.16) by the mole fraction $N_2 = n_2/(n_1 + n_2)$:

$$N_2\frac{d\underline{v}}{dN_2}=-\frac{dV}{dn_1}+\frac{V}{n_1+n_2} \tag{7.17}$$

but the first term on the right-hand side of this equality is the partial molar volume of the first substance, $\bar{v}_1$, and the second term is equal to the molar volume of the solution, $\underline{v}$. Equality (7.12) is thus proved. In an analogous way, we can prove the rule of intercepts for the second component, i.e., that $\bar{v}_2 = \overline{A'B'}$.

The partial molar volume is close in physical meaning to the apparent molar volume $\underline{v}$, which is determined as follows. As before, let a solution contain n_1 moles of solvent and n_2 moles of solute. The total volume of the solution is V and the molar volume of the solvent is $\underline{v}_{01}$. We can subtract the volume of the solvent from the volume of the solution, i.e., we can write $V - n_1\underline{v}_{01}$. This difference is assumed to refer to the volume of the solute. If we divide it by n_2, we shall obtain the apparent molar volume of the solute:

$$\underline{v}_2=\frac{V-n_1\underline{v}_{01}}{n_2} \tag{7.18}$$

This quantity is related to $\bar{v}_2$ in almost the same manner as the ratio of finite differences is related to the corresponding derivative, say, as the mean heat capacity to the true heat capacity.

The apparent volume is not difficult to determine for solutions of various concentrations. For solutions of sodium chloride in water which have different molalities m the following values have been obtained:

m	0	0.1	0.2	0.3	0.4	0.5	1.0
v_{NaCl}, cm^3/mole	16.63	17.20	17.44	17.63	17.80	17.94	18.52

The first figure in this series of increasing numbers has been obtained by extrapolation to zero concentration. The series given above can be described by an empirical formula:

$$\underline{v}_2 = \frac{V - n_1 v_{01}}{n_2} = 16.6253 + 1.7738 n_2^{1/2} + 0.1194 n_2 \tag{7.19}$$

where $n_2 = m$ is the number of moles of NaCl per 1000 g of water and $n_1 = 1000/18 = 55.51$. Solving Eq. (7.19) for the volume of the solution, we obtain:

$$V = 55.51 \underline{v}_{01} + 16.6253 n_2 + 1.7738 n_2^{3/2} + 0.1194 n_2^2 \tag{7.20}$$

Next, in order to find the partial molar volume of NaCl it remains to differentiate V with respect to n_2:

$$\bar{v}_2 = \frac{\partial V}{\partial n_2} = 16.6253 + \frac{3}{2}\, 1.7738 n_2^{1/2} + 2 \times 0.1194 n_2 =$$
$$= 16.6253 + 2.6607 n_2^{1/2} + 0.2388 n_2$$

At $n_2 = m = 0.5$ we obtain the partial molar volume of NaCl, $\bar{v}_2 = 18.63$ cm^3, which can be compared with the apparent molar volume, $v = 17.94$. What has been said above may be regarded as an illustration of the analytical method of determining a partial molar quantity, namely the volume, which is chosen for the sake of clarity. The methods under discussion are in principle, suitable for the calculation of the partial molar quantities of any extensive property of a solution.

The partial molar quantities of extensive properties play the same role for solutions as do the molar quantities for one-component systems. Perhaps, the most important partial molar quantity is the partial molar Gibbs free energy, $\bar{G}_i$, which is identically equal [as known from Eq. (5.164)] to the chemical potential of the component:

$$\bar{G}_i = \mu_i = \left(\frac{\partial G_{\mathrm{total}}}{\partial n_i}\right)_{p,\, T,\, n_j \neq n_i} \tag{7.21}$$

As can be shown, the equations, that have been derived earlier for the molar quantities of individual substances hold for partial molar quantities:

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{p,\, n_i} = -\bar{S}_i \tag{7.22}$$

$$\left(\frac{\partial \bar{G}_i}{\partial p}\right)_{T,\, n_i} = \bar{v}_i \tag{7.23}$$

Since $\overline{G}_i = G_i^\circ + RT \ln f_i$, it follows that

$$\left(\frac{\partial \ln f_i}{\partial p}\right)_{T,n_i} = \frac{\overline{v}_i}{RT} \tag{7.24}$$

and, finally, we arrive at the analogue of formula (5.243)

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{p,n_i} = \frac{H_i^\circ - \overline{H}_i}{RT^2} \tag{7.25}$$

where H_i° is the molar enthalpy of the component in its standard state.

We shall now derive some equations that provide relationships between partial molar quantities and between these quantities and concentrations. These equations are important elements of the mathematical apparatus of the thermodynamic theory of solutions. If the total value of any extensive property of a solution is given by

$$y = f(p, T, n_1, n_2, n_3, \ldots) \tag{7.26}$$

where y may be identically equal to v, U, G, S, etc., then its increment can be expressed by a differential:

$$dy = \left(\frac{\partial y}{\partial p}\right)_{T,n_j} dp + \left(\frac{\partial y}{\partial T}\right)_{p,n_j} dT + \left(\frac{\partial y}{\partial n_1}\right)_{p,T,n_j \neq n_1} dn_1 + \\ + \ldots + \left(\frac{\partial y}{\partial n_i}\right)_{p,T,n_j \neq n_i} dn_i + \ldots \tag{7.27}$$

If the system is studied at constant pressure and temperature and we take into account the definition of partial molar quantities written for the volume (7.7), relation (7.27) can be written as

$$dy = \overline{y}_1\, dn_1 + \overline{y}_2\, dn_2 + \ldots + \overline{y}_i\, dn_i + \ldots \tag{7.28}$$

Here dy may also be considered to be the total value of the property y for a small amount of a solution composed of the amounts of the components $dn_1 + dn_2 + \ldots + dn_i + \ldots$. But to the small amount of the solution we can add the same amount of a solution of the same composition and then repeat the procedure again and again until the total amount of the solution becomes finite. In such a case, the partial molar quantities do not change. An essential point here is that the partial molar quantities depend not on the amount of the solution but on the ratio of the components. Therefore, keeping this ratio constant, we can regard the summation procedure mentioned above as the integration of Eq. (7.28) from 0 to y and over dn_i from 0 to n_i at fixed $\overline{y}_i$:

$$y = \overline{y}_1 n_1 + \overline{y}_2 n_2 + \ldots + \overline{y}_i n_i + \ldots \tag{7.29}$$

Thus, any extensive property of the solution can be represented as the sum of the properties of the components*. But this only looks like an additivity because $\bar{y}_i$ is not a property of a pure component taken separately but, so to say, its manifestation in the solution. In other words, the partial quantities are in fact the properties of the solution and depend on its composition.

If we now visualize the simultaneous change in both n_i and $\bar{y}_i$, then Eq. (7.29) should be differentiated with respect to both variable quantities:

$$dy = \bar{y}_1\, dn_1 + n_1\, d\bar{y}_1 + \bar{y}_2\, dn_2 + n_2\, d\bar{y}_2 + \ldots + \bar{y}_i\, dn_i + n_i\, d\bar{y}_i + \ldots \tag{7.30}$$

We compare this relation with Eq. (7.28). This gives

$$n_1\, d\bar{y}_1 + n_2\, d\bar{y}_2 + n_i\, d\bar{y}_i = \sum n_j\, d\bar{y}_j = 0 \tag{7.31}$$

We now divide Eq. (7.31) by the sum of the moles of the components of the solution, $\sum n_j$:

$$N_1\, d\bar{y}_1 + N_2\, d\bar{y}_2 + \ldots + N_i\, d\bar{y}_i = 0 \tag{7.32}$$

where N_i are the molar fractions of the components. Equations (7.29), (7.31) and (7.32) are known as the *Gibbs-Duhen equations*. They relate the partial molar quantities to the composition of the solution.

Equation (7.32) can be modified by dividing, first, by dN_1:

$$N_1 \left(\frac{\partial \bar{y}_1}{\partial N_1}\right)_{p,\,T} + N_2 \left(\frac{\partial \bar{y}_2}{\partial N_1}\right)_{p,\,T} + \ldots + N_i \left(\frac{\partial \bar{y}_i}{\partial N_1}\right)_{p,\,T} + \ldots = 0 \tag{7.33}$$

Second, it is used for binary solutions (such solutions are most frequently dealt with in the literature) when $N_1 + N_2 = 1$ and $dN_1 = -dN_2$. In this case, the following version of the Gibbs-Duhem equation is used:

$$N_1 \left(\frac{\partial \bar{y}_1}{\partial N_1}\right)_{p,\,T} = N_2 \left(\frac{\partial \bar{y}_2}{\partial N_2}\right)_{p,\,T} \tag{7.34}$$

Applying Eq. (7.31) to a binary solution, we write it for the chemical potentials of the components, which are, by the definition (5.163), the partial molar Gibbs free energies, i.e., $\mu_j = \bar{G}_j$. So, Eq. (7.31) transforms to the following equation:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{7.35}$$

or

$$d\mu_1 = -\frac{n_2}{n_1}\, d\mu_2 = -\frac{N_2}{N_1}\, d\mu_2$$

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* The relations considered here were derived in Chapter 1 (Sec. 1.2) on the basis of Euler's theorem on homogeneous functions.

Of special interest is the application of the last equation to a vapour at equilibrium with a solution. The chemical potential of a component in the vapour and also in the liquid solution is related, by definition, to the fugacity of this component in the vapour, (5.231):

$$\mu_j = \mu_j^\circ + RT \ln f_j$$

In view of this relation, Eq. (7.35) can be rewritten as follows:

$$d \ln f_1 = -\frac{N_2}{N_1} d \ln f_2 \qquad (7.36)$$

This is also one of the forms of the Gibbs-Duhem equation. And, finally, in those cases when the vapour being in equilibrium with the solution may be regarded as a mixture of ideal gases, we obtain the following relation, replacing the fugacity by the pressures:

$$d \ln p_1 = -\frac{N_2}{N_1} d \ln p_2 \qquad (7.37)$$

which is known as the *Duhem-Margules equation.*

Some of the equations given here will be used for the derivation of the regularities describing the behaviour of solutions.

7.3. Ideal Solutions

We shall now be concerned with the study of solutions, and for simplicity we shall first consider ideal solutions. They may be said to be formed by substances similar in chemical nature and, hence, in the nature of intermolecular interaction, say, saturated hydrocarbons such as hexane and heptane, etc. It is exactly because of the similarity of the forces of interaction between identical and different molecules in solution that the formation of such solutions does not involve a change in volume and is not accompanied by a heat effect. This can be illustrated by using Raoult's law. This law refers to the equilibrium between a solution and its saturated vapour:

$$\text{liquid solution} \rightleftharpoons \text{saturated vapour} \qquad (7.38)$$

The vapour in equilibrium with the solution contains all the components of the solution, i.e., is itself a solution. The equilibrium vapour solution may be nonideal, even if the liquid solution is considered to be ideal. The total fugacity of the vapour and the fugacities of the individual components depend on temperature and the composition of the solution. If the temperature is held constant, the fugacity will depend on the composition alone.

Consider a binary solution, using the notation $N_2 = N$ for the mole fraction of the solute in the solution; the mole fraction of the solvent will then be $N_1 = 1 - N$. Experiment shows that, first, the partial fugacity of the vapour of a component above the solution is always lower than the fugacity above a pure component. Second, according to Raoult's generalized law, the fugacity of a component of an ideal solution at all concentrations is proportional to its mole fraction in the solution:

$$f_i = f_{0i}N_i \text{ or } f_2 = f_{02}N \text{ and } f_1 = f_{01}(1 - N) \qquad (7.39)$$

where f_{0i} is the fugacity of a pure component at the vapour pressure of the solution: this quantity is constant at constant temperature and pressure. It should be emphasized that the solution is not ideal if relations (7.39) do not hold over the entire range of concentrations.

Substituting f_i from Eq. (7.39) into Eqs. (7.24) and (7.25) and comparing the result obtained with the corresponding equations for pure substances, we arrive at the following equalities:

$$\bar{v}_i = \underline{v}_{0i} \qquad (7.40)$$

and

$$\bar{H}_i = \underline{H}_{0i} \qquad (7.41)$$

that is, the properties of ideal solutions, such as the molar volume and enthalpy, are independent of the composition of the solution.

This has already been mentioned at the beginning of this section. Formula (7.39) is called *Raoult's law*. The point is that Raoult himself derived his law in 1886 in a simpler form which derives from Eq. (7.39) for a case where a vapour may be regarded as a mixture of ideal gases. Then the equation becomes:

$$p_i = p_{0i}N_i \qquad (7.42)$$

that is, the partial vapour pressure of any component over the solution is equal to its mole fraction in the solution multiplied by the vapour pressure above the pure component. The observations made by Raoult referred primarily to solutions of involatile substances in volatile solvents. Applying Eq. (7.42) to a solvent, we write the relative lowering of the vapour pressure of the solvent above the solution:

$$\frac{p_{01} - p_1}{p_{01}} = N \qquad (7.43)$$

which is seen to be equal to the *mole fraction of the solute.*

Let us apply Raoult's law in the form (7.42) to solutions of two infinitely miscible liquids. The second component will be assumed to be the solute. The partial vapour pressure for the solute is written in the form:

$$p_2 = p_{02}N_2 = p_{02}N \qquad (7.44)$$

The total vapour pressure P is expressed by combining Eqs. (7.43) and (7.44), i.e.,

$$p = p_{01}(1 - N) + p_{02}N \qquad (7.45)$$

Figure 7.2 presents the results of a study of solutions of benzene and dichloroethane. From this figure it is seen that both the partial and total pressures are expressed by straight lines, which means that the solutions obey Raoult's law in the simplest form given, (7.42) to (7.45). Below are given some data for the system propylene dibromide ($C_3H_6Br_2$)-ethylene dibromide ($C_2H_4Br_2$) at a temperature of 85°C:

$N_{C_3H_6Br_2}$ (fractions)	$p_{C_3H_6Br_2}$ (mm Hg)	$\frac{p}{N} = p_0$
0.2221	29.4	132.2
0.4180	52.9	126.6
0.8005	102.5	128.0
1.0000	127.2	127.2

All the figures in the last column must be equal to 127.2, i.e., to the vapour pressure of the pure component. In fact, there are observed deviations to both sides, but they are insignificant.

An important experimental fact that stands out throughout the theory of solutions consists in that the composition of a vapour differs from the composition of a liquid solution. It would be a mistake if we consider such a difference to be a manifestation of nonideality or a deviation from Raoult's law. On the contrary, it is exactly in the case of large deviations that the compositions of vapour and liquid coincide. Let us consider this problem for a system that conforms to Raoult's law. On the basis of Eqs. (7.42) and (7.44) we can write the ratio of the partial pressures of the components of the vapour:

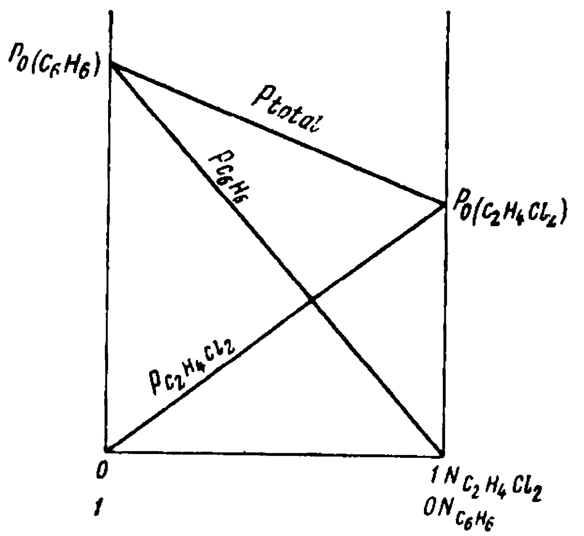

Fig. 7.2. The applicability of Raoult's law to the system benzene-dichloroethane (t = 50°C).

$$\frac{p_2}{p_1} = \frac{p_{02}N}{p_{01}(1-N)} = \alpha \frac{N}{1-N} \tag{7.46}$$

where α is used to denote the ratio p_{02}/p_{01}, which may be called the relative escaping tendency of the second component. Let the mole fraction of component 2 in the vapour be equal to $y \neq N$. Then, according to Dalton's law of partial pressures (5.179), the ratio of the partial pressures can be expressed in a different form:

$$\frac{p_1}{p_2} = \frac{y}{1-y} \tag{7.47}$$

Solving Eqs. (7.46) and (7.47) for y, we obtain

$$y = \frac{\alpha N}{1+(\alpha-1)N} \tag{7.48}$$

from which it can be seen that, in a general case, for solutions that obey Raoult's law the vapour composition will coincide with the composition of the liquid at $\alpha = 1$, i.e., when $p_{02} = p_{01}$. The vapour pressure may be equal for substances which are chemically and physically similar, say, in the case of stereoisomers. But generally the dependence $y = f(N)$ is expressed, in accordance with Eq. (7.48), by a hyperbolic curve, such as the one shown in Fig. 7.3 for $\alpha = 3$.

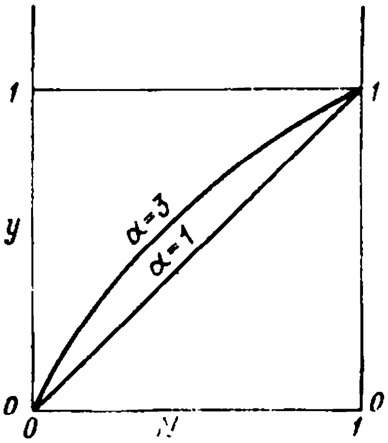

Fig. 7.3. The disagreement between the vapour composition and the liquid composition for systems obeying Raoult's law:

N and y are, respectively, the molar fractions in the liquid and in the vapour.

Let us now return to Raoult's law in the generalized form (7.39) and write it for a solvent:

$$f_1 = f_{01}N_1 = f_{01}(1-N) \tag{7.49}$$

Solutions that conform to Raoult's law in this form are called ideal or perfect. If relation (7.49) is valid for the solvent (component 1), then it can be shown to hold for the solute as well. As a matter of fact, based on the Gibbs-Duhem equation (7.36), we can write:

$$d\ln f_2 = -\frac{1-N}{N}\, d\ln f_1 \tag{7.50}$$

Or, substituting f_1 from Eq. (7.49) into Eq. (7.50),

$$d\ln f_2 = \frac{1-N}{N}\,\frac{dN}{1-N} = d\ln N \tag{7.51}$$

we have:

$$\ln f_2 = \ln N + \ln k$$

or

$$f = kN \tag{7.52}$$

But if the basic equation for f_1, (7.49), does hold throughout the complete range of concentrations, then at $N = 1$ $f_2 = f_{02}$, instead of (7.52), we obtain Raoult's law for component 2, i.e.,

$$f_2 = f_{02}N \tag{7.53}$$

which was required to prove.

For nonideal solutions the proportionality factor k in formula (7.52) differs from f_{02}, i.e., Raoult's law does not hold for the solute.

Relation (7.52) can be used for the solubility of a gas in a liquid. In this case, if the gas pressure p is not very high, it can be substituted for the fugacity:

$$p_2 = kN \tag{7.54}$$

In this form the relation expresses Henry's law (1803), which states that *at constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid.* The proportionality factor k is called *Henry's law constant.*

7.4. Deviations from Raoult's Law

There are often observed both positive and negative deviations from Raoult's law. Figure 7.4 presents some examples of deviations from Raoult's law: the system carbon disulphide-methylal (a large positive deviation) and the system acetone-chloroform (a large negative deviation).

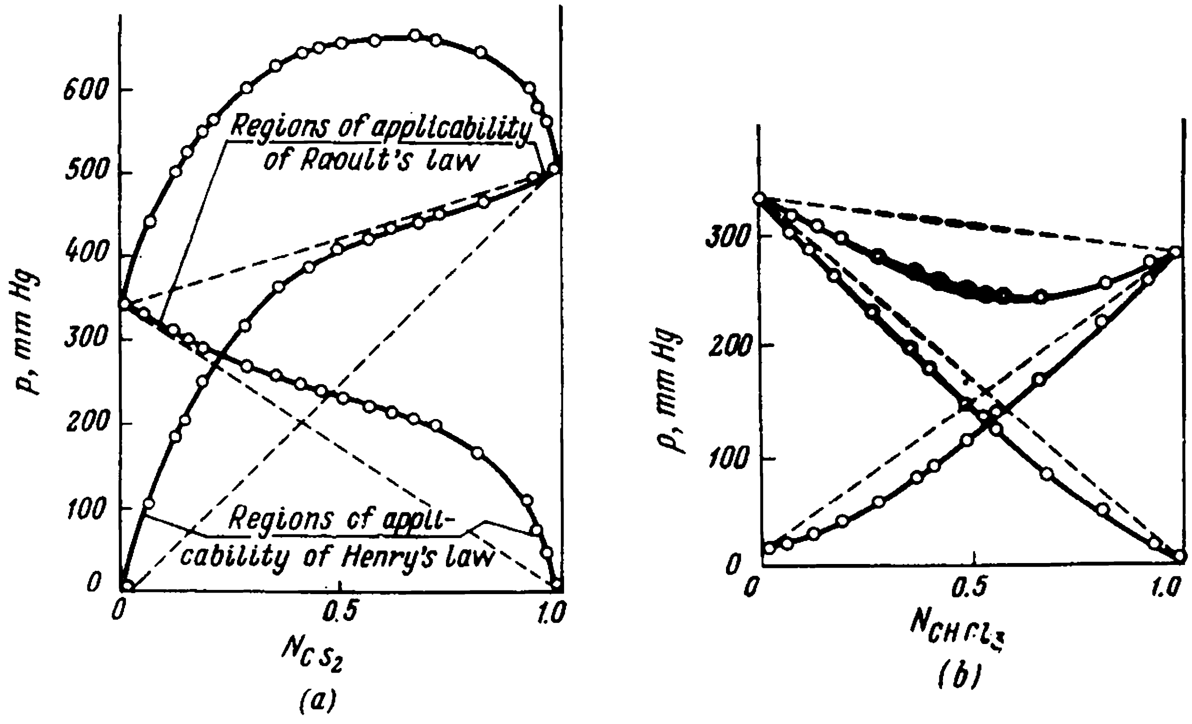

Fig. 7.4. Examples of systems deviating from Raoult's law:
a—the system carbon disulphide-methylal [$CH_2(OCH_3)_2$]; b—the system chloroform-acetone

The graphs of Fig. 7.4 also show the regions of applicability of the laws of the infinitely dilute solutions—the curves of the partial pressures for small additions of solute merge with the straight lines, which express Raoult's law (7.42) to (7.44); these are the regions of the infinitely dilute solutions (see also page 330).

As has already been pointed out, Raoult's law is obeyed by solutions of substances which are similar in their chemical nature (homologues, stereoisomers, isotopically substituted compounds, say, C_6H_6 and C_6D_6). In solutions of such substances the forces of interaction between pairs of like molecules and pairs of unlike molecules are almost the same and addition of one of the components does not affect the total force of intermolecular interaction.

Deviations from Raoult's law are observed in solutions of substances which differ strongly in their properties. In such solutions the forces of intermolecular interaction between like and unlike molecules may be essentially different. If pairs of unlike molecules attract each other more weakly than pairs of like molecules, then the mixing of the substances weakens the total intermolecular interaction. As a result, the evaporation of the molecules from the solution is facilitated. The vapour pressure in this case will be higher than that stipulated by Raoult's law, i.e., there is observed a positive deviation. On the contrary, if the unlike molecules attract each other more strongly than the like molecules, then the mixing enhances the total molecular interaction and the evaporation of the molecules becomes difficult and the result is a negative deviation from the law.

Van Laar, whose works are devoted mainly to the theory of solutions, proposed a formula which combines Raoult's law and the cases of deviations from it. Namely, the partial vapour pressure for a solute is given by

$$p_2 = p_{02} N e^{(1-N)^2 \frac{\Delta U^\circ}{kT}} \tag{7.55}$$

where p_2, p_{02} and N have the previous meaning; k is Boltzmann's constant; T is the temperature; ΔU° is the so-called *interaction energy*, which takes account of the difference in the nature of the interaction of like and unlike molecules. To explain the physical significance of ΔU° reference should be made to Fig. 7.5. The left part of this figure shows the "dissimilar configuration". With an arbitrarily chosen coordination number (6) two unlike molecules are surrounded each by unlike molecules. The right part of the figure is the "similar configuration". The energies of the two systems shown are different—according to van Laar, the interaction energy is half of the difference between the energies of these configurations: $\Delta U^\circ = 1/2\,(\varepsilon_{II} - \varepsilon_I)$. If $\Delta U^\circ = 0$, which means the equality of the forces of interaction of like and unlike pairs, the exponential becomes equal to unity and formula (7.55) changes to Raoult's law. At $\Delta U^\circ > 0$ the deviations are positive and at $\Delta U^\circ < 0$ they are negative. Relation (7.55) cannot, however, be regarded as a theoretical quantitatively regularity since it is very difficult to calculate the interaction energy. Here, one must have made some assumptions as to the coordination number of short-range order and the dependence of the forces on the distance between molecules. All this refers rather to potentialities. But the procedure can be reversed, namely; one can determine ΔU° from experimental data, in which case ΔU° will assume the

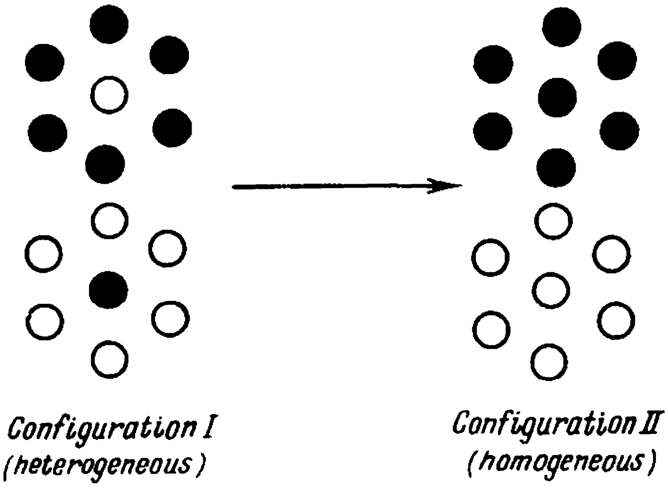

Fig. 7.5. Explaining the concept of exchange in a solution (ΔU°).

character of a certain empirical coefficient. Below are given the values of the coefficient $\beta = \Delta U^\circ/kT$, which have been found in this way for the solutions considered above:

T, K	Component I	Component II	β
323.15	$C_2H_4Cl_2$	C_6H_6	0
308.32	CS_2	$CH_2(OCH_3)_2$	+0.673
308.32	$CHCl_3$	$(CH_3)_2CO$	−0.927

7.5. Limited Solubility of Liquids

Let us rewrite the van Laar equation (7.55), expressing the relative vapour pressure of a component of a binary solution:

$$\frac{p}{p_0} = Ne^{(1-N)^2\beta} \tag{7.56}$$

and calculate the value of p/p_0 as a function of N at different values of β. The results of calculations are given in Fig. 7.6. Of greatest interest is the appearance of a horizontal portion in the curve for $\beta = 2$ and of curves with a maximum and a minimum at $\beta > 2$. This means that the value of $\beta \approx 2$ is the largest of those which have physical meaning for a homogeneous solution since at large values the equation allows for the existence of two or even three solutions having different compositions and the same partial pressure, which is impossible in the presence of a single phase. The equal vapour pressures of the component are however possible when a new phase is formed; while the previous phase was a solution of the second component in the first, the new phase will be a solution of the first component in the second. Thus, the appearance of a maximum on the theoretical curve of the function (7.56) in fact signifies limited solubility and the possibility of separation of the solution into two phases. In Fig. 7.6 the point A represents the concentration of the solution saturated with one of the components. Hence, the van Laar equation allows one to approach the definition of the *critical solution temperature* or the *consolute temperature*. In general, a distinction is made between the upper, or maximum, consolute temperature and the lower, or minimum consolute temperature; *these are temperatures above and below which the substances mix in all proportions.* Equation (7.56) provides the condition only for the upper consolute temperature $T_c : \beta = \Delta U°/kT_c = 2$ or

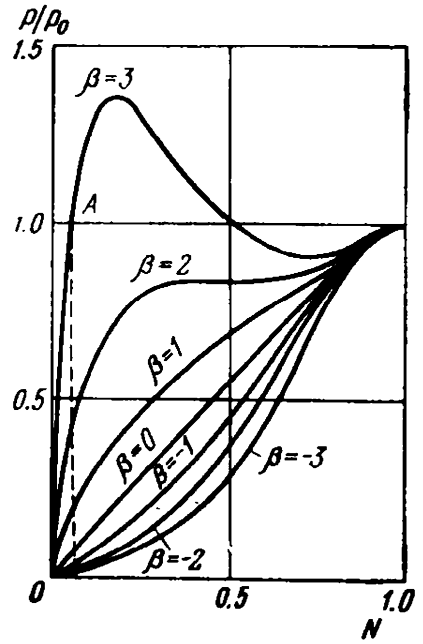

Fig. 7.6. Dependence of the relative vapour pressure of a component of a binary solution on its molar fraction for various values of $\beta = \Delta U°/kT$.

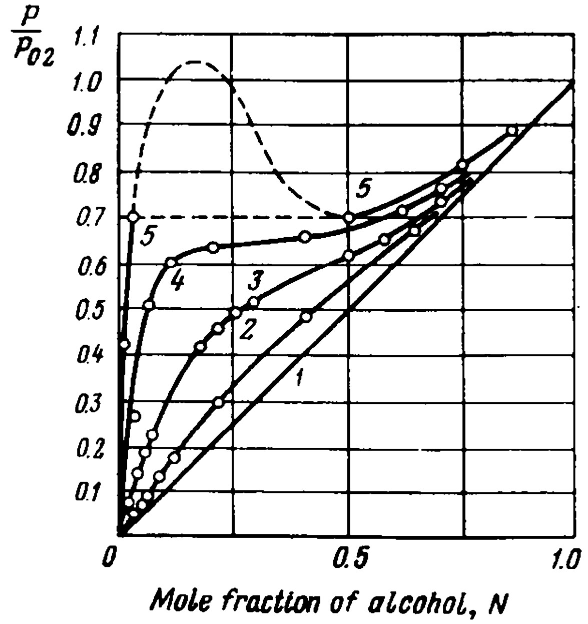

Fig. 7.7. The relative vapour pressure of alcohols above aqueous solutions at 25°C:

1—ideal solution; 2—methyl alcohol (methanol); 3—ethyl alcohol (ethanol); 4—propyl alcohol (propanol); 5—butyl alcohol (butanol).

$$T_c = \frac{\Delta U°}{2k} \qquad (7.57)$$

The upper consolute temperature T_c cannot yet be calculated with sufficient accuracy because of the difficulties that arise in the calculation of the interaction energy. The following considerations are therefore of interest. The value of $\beta = \Delta U°/kT_c$ that determines a deviation from Raoult's law and the onset of limited solubility may vary under the influence of two factors. The first factor is associated with the change in temperature at constant ΔU°. The second manifests itself at constant temperature due to the change in the nature of the interaction between pairs of like and unlike molecules, i.e., ΔU°. In both cases, β may reach a critical value equal to 2. We shall consider in more detail the second case where the gradual change of the properties of the solute in going along the homologous series leads to limited solubility.

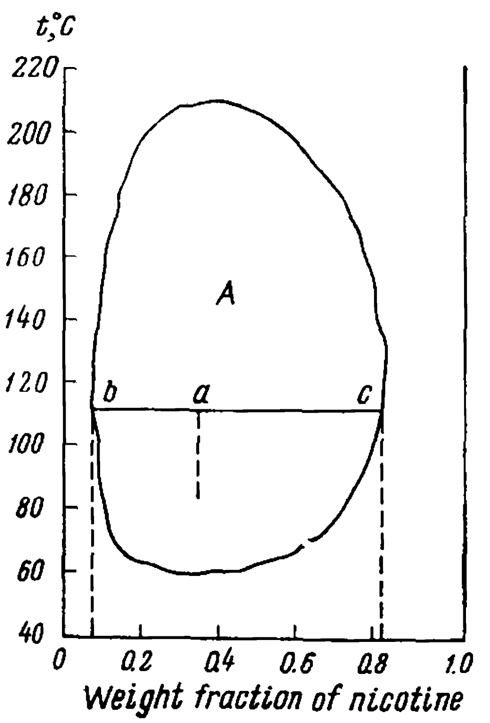

Fig. 7.8. Curve of mutual solubility of nicotine and water with two critical solubility points:

A—phase separation region; at point *a* the system separates into two layers of compositions *b* and *c*; the amounts of the two solutions are determined by the lever rule.

Figure 7.7 shows the curves of the relative vapour pressure of methanol, ethanol, propanol and butanol above aqueous solutions at 25°C versus their mole fractions N. It is seen that in the series C_1-C_3 the deviation from Raoult's law increases and that butanol becomes partially miscible. As the temperature is raised (as the value of β decreases to values lower than 2) the solubility of this alcohol also becomes complete. Hence, the system water-butanol exhibits an upper consolute temperature. It should be admitted in general that the picture observed (Fig. 7.7) resembles the results of the calculation based on the van Laar equation (see Fig. 7.6). The phenomenon may be more complicated in general and, apart from the upper critical solution temperature, there may appear a lower critical temperature. An example is the system nicotine-water [β(N-methyl-α-pyrrolidyl)-pyridine] (Fig. 7.8).

Raoult's law may also prove suitable for nonideal solutions and, more exactly, for a solvent if the concentration of the solute is small. Such solutions are called *infinitely dilute solutions*. A binary infinitely dilute solution is defined by the condition

$$N_1 \to 1, \ N_2 \to 0 \qquad (7.58)$$

In such solutions there is no interaction between solute molecules since they are separated by a large number of solvent molecules and interact only with the latter. Therefore, adding more solvent to such a solution at constant temperature will produce no detectable change in the internal energy or enthalpy, i.e., the dilution is not accompanied by a heat effect and

$$\left(\frac{\partial U}{\partial v}\right)_T = 0 \tag{7.59}$$

A certain analogy is seen in this with an ideal gas, one of the characteristics of which is also a relationship of the type (7.59). It should be borne in mind that the addition of more solute to a dilute solution will in general be accompanied by a heat effect if the solution is not ideal in this respect.

Returning to Raoult's law, let us again refer to Fig. 7.4*a*. From this figure we can see that the vapour pressure of methylal at small concentrations of carbon disulphide undergoes change along a straight line conforming to Raoult's law; the same can be said about the vapour pressure of carbon disulphide at small concentrations of the ester. Figure 7.4*a* shows the regions of applicability of Raoult's law. This is the region of the infinitely dilute solutions. At the same time, for the solute, in accordance with Eqs. (7.50) through (7.52), Henry's law in the form (7.52) or (7.54) holds true. In such cases, for a nonideal solution Henry's law constant k differs from the fugacity of a pure substance, f_{02}. Figure 7.4*a* also shows the regions of applicability of Henry's law. The analogy between a substance in an infinitely dilute solution and an ideal gas is extended by van't Hoff's law which establishes the relationship between the osmotic pressure, the solution concentration (molarity) and the temperature. As we know, if the solution and the solvent are separated by a semipermeable membrane*, the phenomenon of osmosis occurs—the solvent passes through the membrane into the solution. The process of osmosis can be stopped by the excess pressure on the solvent which is just enough to halt the movement and is called the *osmotic pressure*. Treating the data obtained by Pfeffer, van't Hoff arrived at the relation

$$\Pi \underline{v} = RT \tag{7.60}$$

where Π is the osmotic pressure; $\underline{v}$ is the volume of the solution containing 1 mole of solute; T is the absolute temperature; and R is the universal gas constant. Van't Hoff's law is also written in the form

$$\Pi = cRT \tag{7.61}$$

where c is the molarity of the solution. Relation (7.60) is analogous to the ideal-gas law, which forms the basis for the derivation of many thermodynamic relations, say, the law of mass action and the associated formulas. Therefore, these thermodynamic relations derived with the aid of the ideal-gas law are also applicable to infinitely dilute solutions.

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* Burnt clay subjected to special treatment.

7.6. Distillation of Binary Liquid Solutions

Returning to the cases of unlimited solubility (complete miscibility) of two liquids, note that in Chapter 7 (see pages 324, 325, 328) we considered the vapour pressure being dependent on the composition of a liquid solution, N. At the same time, it was pointed out that the composition of the liquid is different from that of the vapour [Eq. (7.48)]. If Raoult's law is obeyed or the deviations from it are not too large, the vapour will contain a larger amount of the volatile component ($\alpha > 1$). But, as will be clear from what follows, this is not always the case. Further in the text we shall plot the dependence of the saturated vapour pressure of the solution both on the composition of the liquid (the mole fraction of the second component N) and on the composition of the vapour (the mole fraction of the second component y) (Fig. 7.9). Such diagrams are called *pressure-composition diagrams.* In Fig. 7.9 the upper curve represents the dependence $p = f(N)$, i.e., the vapour pressure versus the mole fraction of the second component in the liquid, and the lower curve expresses the dependence of the mole fraction of the same component in the vapour. Each point in such a diagram (a representative point) corresponds to a certain definite pressure and definite mole fractions $N = 1 - N_1$ and $y = 1 - y_1$. The lower area a in the diagram corresponds to the pressures lower than the saturated vapour pressure for a given system of any composition. This area may therefore be regarded as the region of the unsaturated vapour. On the contrary, the representative points of the area which lie at pressures exceeding any saturated vapour pressure of a given system correspond to the conditions of existence of the liquid. Thus, if we proceed from point a_1, i.e., a vapour of composition y_1, and compress it, moving upwards, the vapour becomes saturated at point a_2 with the liquid, whose representative point b_2 corresponds to composition N_1. In other words, when the vapour of composition y_1 is subjected to isothermal compression, the first drops of the condensate will have the composition N_1. On the contrary, if we proceed from a liquid of composition N_1 (the

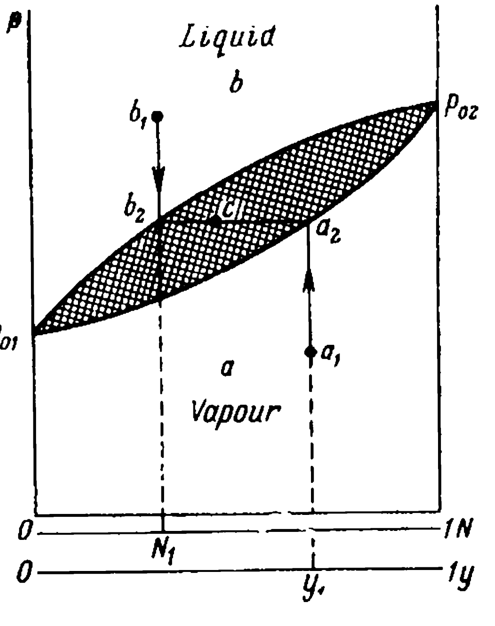

Fig. 7.9. Dependence of the vapour pressure of a binary solution on the liquid composition N and the vapour composition y (T = const).

representative point b_1) and lower the pressure, then at point b_2 there will appear the first traces of the vapour of composition y_1. Stated in a different way, isobars of type a_2b_2 connect the representative points of two phases—the vapour and the liquid which are in equilibrium with each other.* The representative points within the hatched region correspond to systems that separate into two phases—the liquid solution and the vapour in equilibrium with this solution. Thus, at point c the composition of the liquid phase corresponds to point b_2 and the vapour phase to point a_2. The amounts of the coexisting phases are given by the *lever rule* (also known as the *level principle*):

$$\frac{m_{\text{liq}}}{m_{\text{vap}}} = \frac{\overline{ca_2}}{\overline{cb_2}} \qquad (7.62)$$

that is, the masses of the coexisting phases are in the ratio which is inversely proportional to the lengths that are obtained when the representative point c divides the isobar connecting the points of the phases (a_2 and b_2). Instead of the curves expressing the dependence of the vapour pressure on the composition at constant temperature, use is often made of *temperature-composition diagrams*—plots of the boiling point against the composition at constant pressure ($p = 1$ atm). An example of such diagrams is shown in Fig. 7.10; it refers to the system considered in Fig. 7.9. The new diagram is upside-down in relation to the pressure diagram. In this case, the lower area a lying at temperatures below any boiling point is the liquid region, and the upper area b is accordingly the vapour region. The heterogeneous region of separation into phases is enclosed by curves, as before.

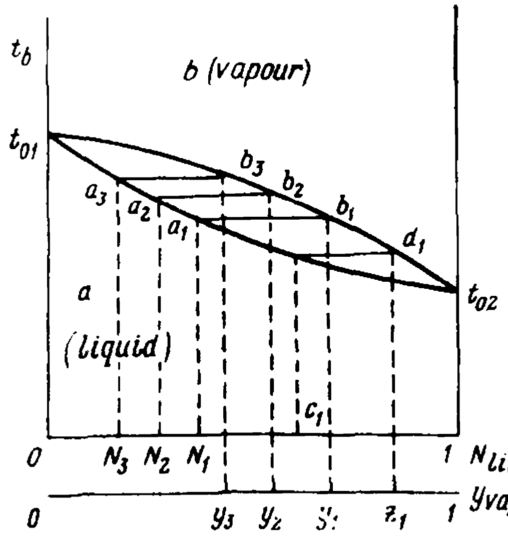

Fig. 7.10. Dependence of the boiling point of a liquid solution on the liquid composition N and the vapour composition y:

The boiling points of the pure components are t_{01} and t_{02}; the field a is the liquid region; the field b is the vapour region. (The graph corresponds to the system shown in Fig. 7.9.)

Let us consider briefly *fractional distillation* which repeats the boiling and condensation cycle several times and can be used to separate a solution completely into its components if only there is no extremum on the curves of $p = f(N)$ or $t_{\text{boil}} = f(N)$. Suppose, for example, that we heat a solution of composition N_1. At point a_1 it begins to boil, the first portion of the vapour having a composition corresponding to point b_1, i.e., the composition y_1. Upon boiling and with the vapour coming off both the solution and the vapour will be enriched in the less volatile component. As the boiling starts we begin to distill the first fraction (fraction I) by condensing the vapour. We discontinue the recovery of fraction I when the composition of the liquid corresponds to N_2 at point a_2. Since the last drop of the condensate has a composition corresponding to point b_2, i.e., the composition y_2, the distillate I will have a composition between y_1 and y_2. Since this will be a liquid solution, we denote its composition by c_1. At point a_2 we start distilling fraction II; the distillation of this fraction is stopped at point a_3, which naturally corresponds to a solution containing a lesser amount of the second component. The composition of fraction II will be between y_2 and y_3. On further boiling the liquid that boils at a higher temperature and the fractions distilled become impoverished in the second component and enriched in the first component. The last drops of the boiling liquid contain the almost pure first component. After the original solution has been separated into fractions we redistill these fractions. Thus, when fraction I of composition c_1 boils, the vapour coming off has a composition corresponding to point d_1, i.e., the vapour is strongly enriched in the second component. In this way, by repeating the distillation of the individual fractions and combining the fractions similar in composition we can eventually separate the solution into the pure components. However, as has already been said, this is possible if the pressure-composition or boiling point-compo-

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* The horizontal line connecting the points a_2 and b_2 is known as a *tie-line*. In general, a tie-line connects the compositions of equilibrium phases.

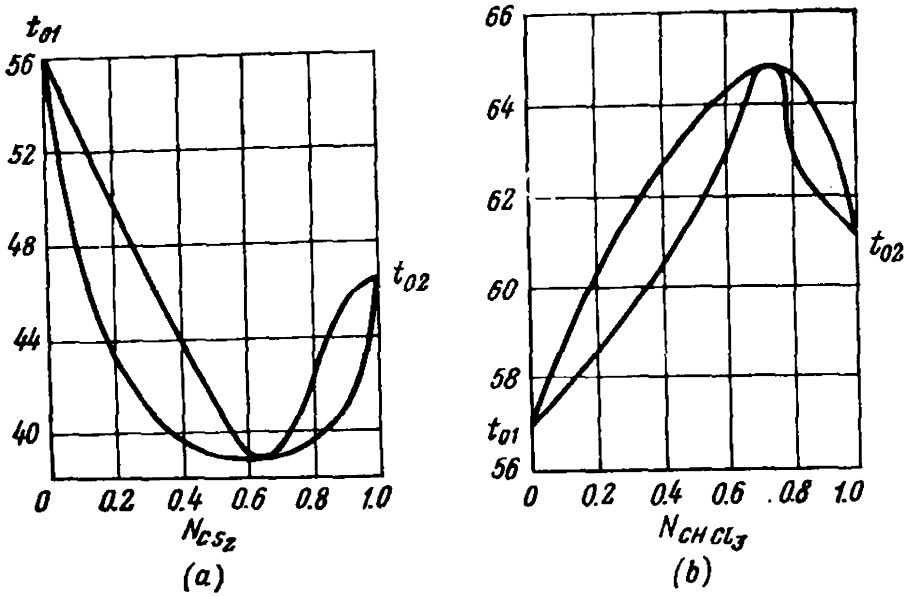

Fig. 7.11. Dependence of the boiling temperature on the composition for binary systems:
a—system $CS_2/CH_2(OCH_3)_2$; b—system $(CH_3)_2CO/CHCl_3$.

sition curves do not exhibit extrema that appear at large deviations from Raoult's law.

Figures 7.11*a* and *b* are diagrams of the boiling point against the composition of liquid or vapour for the systems carbon disulphide-methylal and chloroform-acetone which have been considered earlier (see Fig. 7.4). The minimum and the maximum in these figures correspond, respectively, to the maximum and the minimum in Fig. 7.4.

In connection with the presence of extrema on vapour-pressure (or boiling-point) curves for binary solutions, Gibbs and independently, Konovalov formulated two laws*:

1. *The Gibbs-Konovalov first law*: In the vapour phase there predominates a component whose addition to the solution increases the total vapour pressure (lowers the boiling point).
2. *The Gibbs-Konovalov second law*: The extremal points on total vapour pressure- or boiling point-composition curves correspond to solution-vapour equilibrium states at which the compositions of the two phases become the same.

The two laws can be deduced with the aid of the Gibbs-Duhem-Margules equations. We proceed from Eq. (7.37) which is given here in the following form:

$$(1 - N)\, d \ln p_1 = -N d \ln p_2 \tag{7.63}$$

or

$$(1-N)\frac{dp_1}{p_1} = -N\frac{dp_2}{p_2}$$

and also

$$dp_1 = -\frac{N}{1-N}\cdot\frac{p_1}{p_2}\,dp_2 \tag{7.64}$$

Further, let us denote, as before, the mole fractions of substances in the vapour by $1 - y$ and y. According to Dalton's law,

$$p_2 = py \text{ and } p_1 = p\,(1 - y) \tag{7.65}$$

Substituting relations (7.65) into Eq. (7.64), we obtain

$$dp_1 = -\frac{N}{1-N}\cdot\frac{1-y}{y}\,dp_2 \tag{7.66}$$

The total vapour pressure is equal, according to Dalton's law, to the sum of the partial pressures of the components, i.e.,

$$p = p_1 + p_2 \tag{7.67}$$

or

$$dp = dp_1 + dp_2$$

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* These conclusions are also known as the *Gibbs-Konovalov theorems* (R. S. Berry, S. A. Rice, and J. Ross, *Physical Chemistry*, John Wiley and Sons, New York, 1980).—*Tr.*

Combining Eqs. (7.66) and (7.67), we have

$$dp = \left[1 - \frac{N}{1-N} \cdot \frac{1-y}{y}\right] dp_2 \tag{7.68}$$

and dividing Eq. (7.68) by dN, we write a derivative expressing the dependence of the total vapour pressure on the composition of the liquid:

$$\frac{dp}{dN} = \left[1 - \frac{N}{1-N} \cdot \frac{1-y}{y}\right] \frac{dp_2}{dN} = \frac{y-N}{(1-N)\,y} \frac{dp_2}{dN} \tag{7.69}$$

At the extremal point $(dp/dN) = 0$ and the derivative dp_2/dN is always greater than zero—we have already said (in connection with Raoult's law; see page 323) that the partial vapour pressure of a component above the solution is always lower than the vapour pressure above a pure component. Since the addition of more component makes the solution approach the pure component, from the first postulate there follows the second, i.e., $dp_2/dN > 0$. Thus, the equality of relation (7.69) to zero can be satisfied provided that the expression before the derivative equals zero, i.e.,

$$y = N \tag{7.70}$$

which means that the composition of the liquid is the same as that of the vapour at the extremal point, this coincidence being stated by the Gibbs-Konovalov second law. From relation (7.70) there also emerges the Gibbs-Konovalov first law. If $dp/dN > 0$, i.e., the total vapour pressure increases with addition of the component, but since dp_2/dN is always greater than zero, it follows that

$$y > N \tag{7.71}$$

that is, the vapour contains a predominating amount of that component whose addition increases the total vapour pressure of the solution. From the Gibbs-Konovalov second law it also follows that there is another possibility, namely, the less volatile component predominates in the vapour. For example, from Fig. 7.11 it can be seen that on the portions to the right of the extremum those components predominate in the vapour which have higher boiling points, i.e., the less volatile methylal and chloroform.

Mixtures of liquids corresponding to the extremal points on the curves considered are called *azeotropic mixtures* (or *azeotropes**)—such a mixture boils as though it were a single pure liquid and cannot be separated by distillation. If diagrams of the types shown in Fig. 7.11 are divided into two parts by a vertical line, the part to the right of the azeotrope and the one to the left, it will be clear that a mixture of arbitrary composition can be separated by distillation into an azeotrope and one of the components. Examples of an azeotropic mixture are listed in Table 7.1.

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* Azeotropic mixtures are constant-boiling mixtures. The word *azeotrope* comes from the Greek for "boiling without changing".—*Tr.*

TABLE 7.1. **Selected Two-Component Azeotropes**

I. The first component—H_2O			Azeotrope	
The second component of the azeotrope			boiling point, °C	content of component 1, per cent by weight
formula	name	boiling point, °C		
HCl	Hydrogen chloride	—80	108.58	79.78
N_2H_4	Hydrazine	113.8	120	32.3
CS_2	Carbon disulphide	46.5	43.6	2
$CHCl_3$	Chloroform	61.2	56.2	2.6
C_2H_5OH	Ethanol	78.3	78.174	4.0
$C_2H_5OC_2H_5$	Diethyl alcohol	34.5	34.15	1.26
C_5H_5N	Pyridine	115.3	93.6	41.3
C_6H_5Cl	Chlorobenzene	131.8	90.2	28.4
$C_{10}H_{14}N$	Nicotine	246	99.85	97.48
II. The first component—ammonia		—33.43		
CH_3OCH_3	Dimethyl ether	—23	—37	42.5
C_3H_8	Propane	—42	—44	5-10
C_4H_{10}	Butane	—0.5	—37.1	45
III. The first component—carbon disulphide		—46.25		
C_3H_7Cl	Propyl chloride	46.6	45.2	55
$C_3H_8O_2$	Methylal	42.25	37.25	46
$CH_3COOC_2H_5$	Ethylacetate	76.7	46.1	97

7.7. Boiling and Freezing Points of Solutions of Involatile Substances. Ebullioscopy and Cryoscopy

Raoult's law which was originally deduced in the form (7.43) for solutions of relatively involatile substances in a volatile solvent played an important part in the development of chemistry. From the lowering of the vapour pressure of solvent in solution there emerge important (especially in the historical aspect) regularities associated with the boiling and freezing points of solutions. Figure 7.12 presents curves of vapour pressure versus temperature above a pure liquid and a solid solvent and also curves for the vapour pressure above solutions of various concentrations. As can be seen from this figure, in the case of solutions the curves pass lower than for a pure solvent and intersect the isobar at $p = 1$ atm at higher temperatures. Hence, the dissolution of an involatile substance increases the boiling temperature of the solution. On the other hand, the curves *3*, *4* and *5* intersect the curve *2* at lower temperatures. The point of intersection corresponds to a temperature at which the liquid solution is in equilibrium with the solid solvent, i.e., the freezing point. So, the freezing temperature of the solution* is lower than that of the pure solvent.

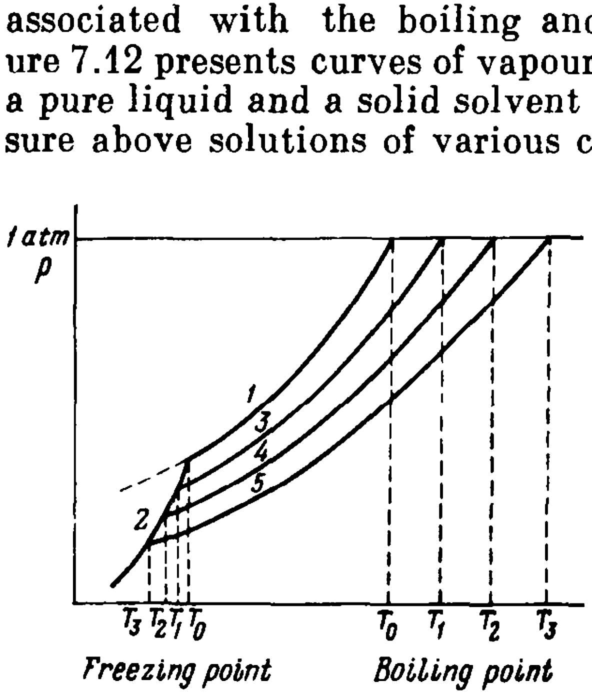

Fig. 7.12. Schematic representation of the dependence of vapour pressure on temperature:

1—pure liquid solvent; *2*—pure solid solvent; *3*, *4*, and *5*—solvent above solutions with increasing concentration of the nonvolatile substance; curves *1*, *3*, *4*, and *5* diverge in moving to the right since $(p_0 - p)/p_0 = \text{const}$ and the difference $p_0 - p$ increases with increasing p_0.

Let us deduce some regularities that relate the boiling-point elevation of solutions and the freezing-point lowering (or freezing-point depression) to the solute concentration. Applying Raoult's law in the simplest form, we write the boiling condition for the solution:

$$p_1 = p_{01} N_1 = 1 \text{ atm} \tag{7.72}$$

where p_1 is the vapour pressure of the solvent; N_1 is its mole fraction in solution. From Eq. (7.72) we derive the following relation:

$$\frac{d \ln p_1}{dT} = \frac{d \ln p_{01}}{dT} + \frac{d \ln N_1}{dT} = 0 \tag{7.73}$$

Next we apply the approximate Clausius-Clapeyron equation (5.18) to the solvent:

$$\frac{d \ln p_{01}}{dT^2} = \frac{\Delta H_{\text{vapn}}}{RT^2} = -\frac{d \ln N_1}{dT} = -\frac{d \ln (1-N)}{dT} \tag{7.74}$$

---

* Here we are dealing only with cases in which only the pure solid solvent separates out once the solution starts freezing.

Multiplying the last expression by dT, we integrate:

$$-\int_0^N d\ln(1-N)=\int_{T_0}^T \frac{\Delta H_{\text{vapn}}}{RT^2}\,dT$$

or, assuming at a first approximation that ΔH_{vapn} is independent of the temperature, we have:

$$-\ln(1-N)=\frac{\Delta H_{\text{vapn}}}{R}\cdot\frac{T_0-T}{T_0T} \tag{7.75}$$

Further, we make use of the expansion of the logarithm into a power series in N, i.e.,

$$-\ln(1-N)=N+\frac{N^2}{2}+\frac{N^3}{3}+\dots$$

and retain, at small N (low concentrations of the solution), only the first term of the series. Then, denoting the boiling-point elevation $T_0 - T$ by ΔT_b, we obtain the following relation instead of (7.75):

$$\frac{\Delta H_{\text{vapn}}}{R}\cdot\frac{\Delta T_b}{T_0T}\approx N=\frac{n_2}{n_1+n_2} \tag{7.76}$$

where n_1 and n_2 are the numbers of moles of the solvent and solute, respectively. Further transformations of expression (7.76) reduce to the following: the small number n_2 (small for a dilute solution) is neglected as compared with n_1; the number of moles of the solvent, n_1, is expressed in terms of the weight of the solvent and its molar mass ($n_1=g_1/M_1$); $g_1=1000$ g is chosen; the product T_0T is replaced tentatively by T_0^2; and the specific heat of vaporization is introduced: L_1, cal/g, ($\Delta H_{\text{vapn}} = L_1M_1$). Now, solving (7.76) for ΔT_b, we obtain:

$$\Delta T_b=\frac{RT_0^2}{L_1 1000}n_2=\left[\frac{RT_0^2}{L_1 1000}\right]m \tag{7.77}$$

where n_2 has been replaced by m, which is the number of moles of solute in 1000 g of solvent (molality). The quantities in square brackets are either the general constants or the constants characterizing a given solvent. We introduce the notation

$$\frac{RT_0^2}{L_1 1000}=E \tag{7.78}$$

The constant E is called the *molal boiling point elevation constant* or the *ebullioscopic constant*. It gives the boiling point increase [calculated from Eq. (7.77)] when 1 mole of substance is dissolved in 1000 g of solvent (molality $m = 1$)*. Thus,

$$\Delta T_b = Em \tag{7.79}$$

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* As a matter of fact, a solution with $m = 1$ does not obey relation (7.77).

and the boiling point elevation of the solution is proportional to molality. Relation (7.79) is known as the ebullioscopic equation.

Using a method similar to the one just described, we can derive another, more important formula, the so-called *cryoscopic formula*, which defines the freezing point lowering of the solution. Namely,

$$\Delta T_f = \frac{RT_0^2}{l_1 1000} m = Km \tag{7.80}$$

TABLE 7.2. **Ebullioscopic and Cryoscopic Constants of Selected Substances**

$$K = \frac{RT_0^2}{l_1 1000}$$

Substance	Melting point, °C	Cryoscopic constant	
		determined experimentally	calculated according to Eq. (7.80)
$BaCl_2$	960	108	108.6
HCl	−112	4.98	—
H_2O	0	1.853	1.859
D_2O	3.82	—	2.05
H_2O_2	−1.07	2.0	1.97
Anthracene	213	11.65	—
Benzene	5.449-5.455	5.065-5.075	5.069
Camphor	178-178.7	39.6-40.0	—
Naphthalene	80.1	6.899	6.98
Acetic acid	16.65	3.9	3.57
CCl_4	−24.7	29.8	—

$$E = \frac{RT_0^2}{L_1 1000}$$

Substance	Boiling point, °C	Ebullioscopic constant	
		determined experimentally	calculated according to Eq. (7.78)
HCl	−82.9	0.64	0.68
H_2O	100.0	0.51-0.52	0.513
H_2S	−60.2	0.63	0.66
Acetone	56.0	1.48	1.762
Benzene	80.2	2.57	2.61
Hexane	68.7	2.78	2.94
Diphenyl	254.9	7.06	—
Diethyl ether	34.6	2.02	—
Camphor	204	6.09	—
Carbon tetrachloride	76.7	5.3	5.24

where l_1 is the specific heat of melting (fusion) of the solvent, cal/g; T_0 is its melting-freezing point, and K is called the *molal freezing point lowering constant* or the *cryoscopic constant.*

As can be seen from Eqs. (7.78) and (7.80), the two constants can be calculated if we know the heat of vaporization and the heat of fusion of a given solvent and also the temperature of the corresponding phase transitions. For practical purposes, however, it is recommended that the experimental values of E and K be used. Table 7.2 gives the constants E and K for some solvents.

The importance of the cryoscopic and ebullioscopic formulas derives from the fact that they make it possible to determine the molar mass of a solute from the freezing point depression and the boiling point elevation of a solution. This explains why these constants have played an important role in the development of chemistry, contributing to the establishment of correct molecular and atomic weights. It should be noted that when determining the boiling point of a solution it is necessary to place the thermometer bulb directly into the solution. When the bulb is in the vapour above the solution, the thermometer will show, as was pointed out by Faraday, the boiling point of the solvent.

Chapter 8

The Phase Rule

8.1. General Concepts and Derivation of the Phase Rule

This chapter is devoted to equilibria in complex heterogeneous systems. We have already dealt with equilibria of this type while studying systems, such as liquid $\rightleftharpoons$ vapour, solid $\rightleftharpoons$ liquid, etc., on the basis of the Clausius-Clapeyron equation (Chapter 5). Equilibria of this kind have also been considered in sections devoted to chemical equilibrium and in Chapter 7. A quantitative treatment of the problem for complex heterogeneous systems is either difficult or simply impossible. Before proceeding to a study of such systems, it will be necessary to define and explain in some detail certain terms which are employed frequently in this connection. *A phase is defined as a part of a system, uniform throughout in chemical composition and physical properties; its thermodynamic properties change continuously from point to point. A phase is separated from other homogeneous portions of the system by boundary surfaces, where the properties undergo a discontinuous change.* This definition differs from the one given earlier by specifying the possibility of a continuous change of the properties. Imagine, for example, a vertically placed tube, at the bottom of which there is a certain amount of a liquid with the vapour above it. Because of the influence of the force of gravity the vapour pressure varies with the level height* in accordance with the relation known as the Laplace barometric formula; this formula is derived from the more general Boltzmann equation (6.76):

$$p = p_0 e^{-mgh/kT} \tag{8.1}$$

where p_0 and p are, respectively, the pressures at zero height and height h; m is the mass of the molecule; g is the acceleration due to gravity. Such a vapour with its pressure changing with height constitutes a single phase. As an example of a simple multiphase system may be given the system "water" consisting of ice, liquid water and water vapour which coexist in equilibrium with each other. There are three phases in this system. A mass of ice crystals forms a separate solid phase; the liquid, including the possible drops on the walls and lid of the vessel, is a second phase; the third phase is the vapour. In general, a vapour or a mixture of vapours or gases, being a homogeneous system, forms, as a rule, a single phase.* For instance, in a heterogeneous equilibrium described by the reaction equation

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* In the absence of other factors, say temperature gradients, convection.

$$FeO + H_2 \rightleftharpoons Fe + H_2O \text{ (vapour)} \tag{8.2}$$

we can see one vapour-gaseous phase and two solid phases. Metallic iron and its oxide, while not dissolving in each other, exist as separate crystals—as two separate phases. We can imagine the following system: a solid salt at the bottom of the vessel, a saturated solution of the salt above it, and the vapour above the solution. There are three phases in this system. But if we have not one but two (or more) solid salts, say NaCl and $MgSO_4$, these will form two solid phases; the solution saturated with these salts will constitute a single liquid phase and the vapour the third phase.

Another important concept is a *component*. The *number of components* is the minimum number of species necessary to define the composition of the system. The smallest number of components is one; while studying phase equilibria in Chapter 5, we dealt with one-component systems.

In Chapter 7 we were mainly concerned with two-component systems—binary solutions. The minimum number of substances necessary to form a system may be substantially different from the total number of substances present in the system because of the possible interconversions. For example, during the course of the dissociation reaction

$$CaCO_3(\text{sld}) \rightleftharpoons CaO(\text{sld}) + CO_2 \tag{8.3}$$

the minimum number of substances required to form a system of arbitrary composition, i.e., the number of components, equals 2. It might seem that calcium carbonate alone would suffice for the formation of this system containing three substances. In this case, however, it is possible to prepare CaO and CO_2 in strictly definite equivalent proportions. Therefore, in order to form the system (8.3) of arbitrary composition it is necessary to have two components. Here we need not specify which particular substances are chosen as the components of the system: first, this will depend on the conditions of the particular task, and, second, for what follows we are interested not so much in specifying the components as in counting the total number of components. As an example, we may consider a solution of acetic acid in water. This solution contains a large number of various chemical species: H_3O^+, $(H_2O)_2$, CH_3COOH, CH_3COO^-, OH^-

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* Data are available at present on the phase separation of gaseous mixtures at high pressures.

and, possibly, others. We may regard each of these species as a certain particular substance, but it is clear that there are only two components in the system—water and acetic acid.

There exists a rule for counting the number of components: it equals the *number of substances present in the system minus the number of independent equations that relate these substances.* Thus, the system (8.2) contains three components and the system (8.3) has two components. In connection with the rule given we may also regard components as the independent constituent parts of the system. To ascertain the essence of the matter it will be useful to consider a hypothetical system proposed here as a paradox:

$$\begin{tikzcd} A \arrow[r, harpoon, shift left] \arrow[d, harpoon, shift left] & B \arrow[l, harpoon, shift left] \arrow[d, harpoon, shift left] \\ D \arrow[u, harpoon, shift left] \arrow[r, harpoon, shift left] & C \arrow[l, harpoon, shift left] \arrow[u, harpoon, shift left] \end{tikzcd} \tag{8.4}$$

It is said that the number of components in this system is zero since the number of substances is equal to the number of equations. However, as can easily be seen, one equation is superfluous. For example, having written the equilibrium constants in the form

$$K_1 = \frac{[B]}{[A]}; \quad K_2 = \frac{[C]}{[B]}; \quad K_3 = \frac{[D]}{[C]} \text{ and } K_4 = \frac{[A]}{[D]}$$

we see that the fourth equation is a combination of the three other equations, i.e.,

$$K_1K_2K_3 = \frac{[B]}{[A]}\frac{[C]}{[B]}\frac{[D]}{[C]} = \frac{[D]}{[A]} = \frac{1}{K_4}$$

Hence, the system (8.4) would have contained one component.

The third important concept in the theory of phase equilibria is the *number of degrees of freedom* or *variance*. This term is used to denote the *possibility of an arbitrary change of some variable quantity (property) that describes the state of the system without changing the number of phases.* For example, in the case of a one-component and single-phase system, say a gas, we can arbitrarily change two properties: p and T, or p and $\underline{v}$, or $\underline{v}$ and T, without changing the phase state. If we specify only two variables, say the pressure and temperature of the gas, we shall thereby specify the third variable—its molar volume, $\underline{v}$. Thus a pure gas has two degrees of freedom. If the temperature of the gas is lowered so that at a given pressure the condensation of the vapour begins, the two-phase system formed will have only one degree of freedom. For instance, if we specify the temperature, this will fix the saturated vapour pressure and the molar volume. At the so-called *triple point* (see Fig. 5.5) three phases are at equilibrium—solid, liquid, and gas. Such a system can exist only at strictly definite values of temperature and pressure, and these, in turn, will uniquely determine the molar volumes $\underline{v}$ of the substance in all the three states of aggregation, i.e., the system is said to have zero degrees of freedom or to be *invariant*.

The p-v-T diagram for a one-component system (a phase diagram) must naturally have three dimensions. The simplest phase diagram obtains for an ideal gas—this is the only surface (see Fig. 1.3), whose intersections with a constant-temperature plane is a hyperbolic

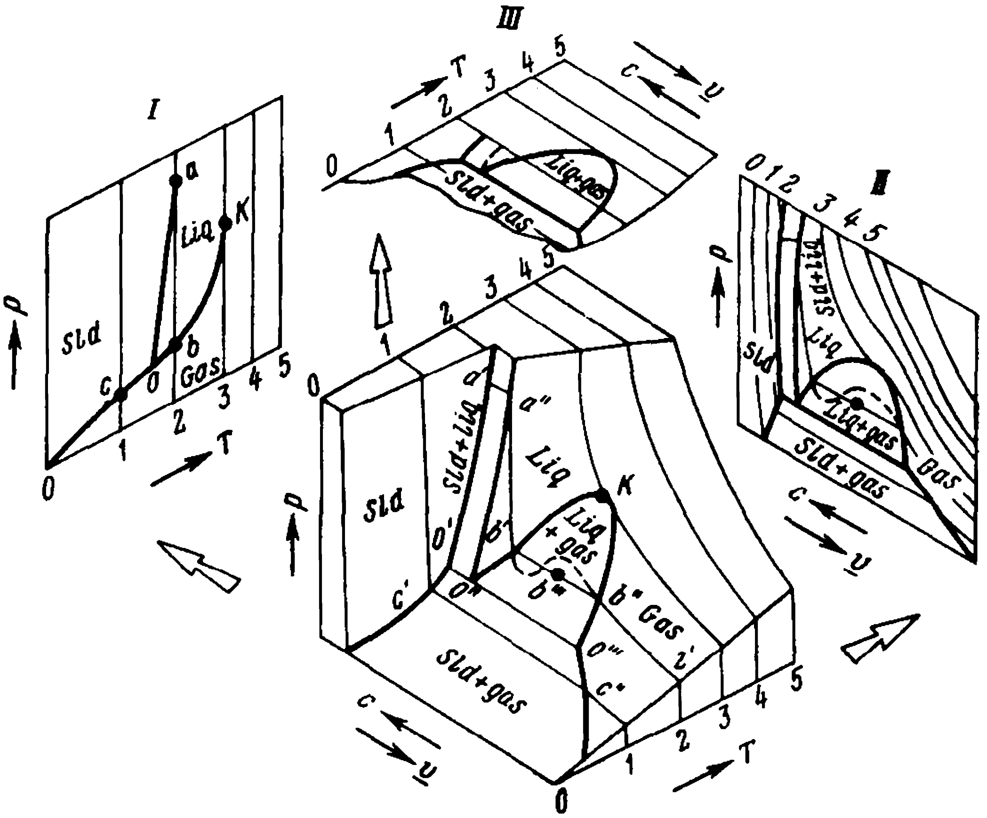

Fig. 8.1. Three-dimensional phase diagram for carbon dioxide and the projections of the diagram on the p-T (I), p-v = $1/c$ (II) and v-T (III) planes.

dependence $pv = RT$ = const—the isotherm of an ideal gas (see Fig. 1.2). The situation for real multiphase systems is considerably more complicated; it is similar to the diagram shown in Fig. 8.1 for a one-component system. This figure shows the surfaces of coexistence of the phases: gas, liquid, and solid. The point K is a critical point and at temperatures corresponding to the isotherms *3*, *4*, *5*, . . ., the p-v-T surface is similar to the one shown in Fig. 1.3. We can distinguish a liquid surface (liq) and a solid surface (sld). The points on these surfaces correspond to systems having two degrees of freedom. There are also surfaces of coexistence of the two phases. Thus, the points of the surface bounded by the line $O''KO''$ correspond to the equilibrium system liquid $\rightleftharpoons$ vapour (gas). Here the system has one degree of freedom and, for example, if we specify the temperature, say the isotherm *2*, the points b' and b'' will give the molar volumes of the gas and liquid phases and the pressure will also be fixed. The representative point of the system b''' can shift at constant temperature within the limits from b' to b'', but this means only a change in the ratio of the amounts of the coexisting phases. Generally, the straight lines on the diagram, namely $a'a''$, $b'b''$, $O'O''O'''$ and $c'c''$, connect the phases that are at equilibrium. Let us trace out the changes in the system described by the movement of the representative point along the isotherm *2*. Proceeding from point *2'*, we

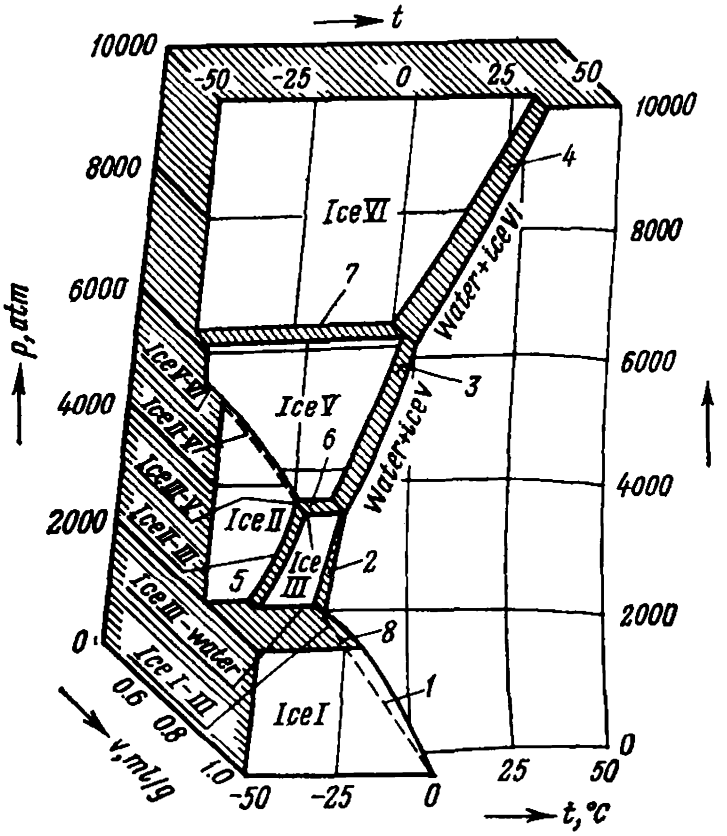

Fig. 8.2. Three-dimensional phase diagram for water in the system of coordinates p, v, T; the phase existence surfaces:
1—ice I-water; *2*—ice III-water; *3*—ice V-water; *4*—ice VI-water; *5*—ice II-ice III; *6*—ice III-ice V; *7*—ice V-ice VI; *8*—ice I-ice III.

compress the system. Up to the point b'' it will remain gaseous, more exactly vapourous, and at the point b'' the vapour will become saturated. Further compression will be associated with the formation of a liquid and the two-phase system liquid $\rightleftarrows$ vapour will coexist up to the point b', where the vapour will disappear. A subsequent decrease in the volume is accompanied by a sharp increase in the pressure from b' to a'' and it means that the liquid is compressed. At point a'' the liquid is already in equilibrium with the solid. Accordingly, along the straight line a'-a'' the liquid and the solid coexist. As the volume is reduced further the solid is being compressed. Apart from the three-dimensional diagram, Fig. 8.1 also shows its projections on the p-T, T-v and p-v planes. The relations between the volumes of the phases are most frequently neglected on phase diagrams and use is made of the projection I on the p-T plane. On this plane the three points O''', O'' and O', for example, which correspond to the vapour, liquid and solid phases in equilibrium, merge into a single triple point O.

Figure 8.2 shows the three-dimensional diagram for water at high pressures, on which there can be seen numerous polymorphic transformations of ice. The diagram is supplemented by Table 8.1 which contains some information on the equilibrium pressures and temperatures for four modifications of ice. As has been pointed out above, the melting point decreases with pressure only for ice I. When the three-dimensional diagrams for water are projected onto the p-T plane, figures are obtained which were considered in Chapter 5, and planar phase diagrams for water at low pressures (see Fig. 5.5) and high

TABLE 8.1. **The Relationship Between the Pressure, Melting Point and the Change of the Volume of Water**

Ice modification	Pressure, atm	Temperature at equilibrium, °C	Δv, cm^3/mole
Ice I	1	0.0	−1.62
	610	−5.0	−1.83
	1130	−10.0	−2.02
	1590	−15.0	−2.195
	1970	−20.0	−2.365
Ice III	2115	−22.0	0.839
	2510	−20.0	0.668
	2910	−18.5	0.542
	3530	−17.0	0.416
Ice V	3140	−20.0	1.48
	3800	−15.0	1.36
	4510	−10.0	1.225
	5440	−5.0	1.086
	6360	0.0	0.95
Ice VI	4790	−15.0	1.765
	6810	−5.0	1.69
	6360	0.0	1.65
	7640	10.0	1.52
	9000	20.0	1.355
	12,319	40.0	1.065
	18,000	66.0	0.764
	22,400	81.6	0.595

pressures (see Fig. 5.7). We shall return to diagrams of this type at a later time.

Thus, there are y components and k phases in the system and it has f degrees of freedom. In 1867 J. W. Gibbs derived a relation connecting these quantities:

$$f = y + 2 - k \tag{8.5}$$

which is known as the *Gibbs phase rule* or simply as the *phase rule*. According to Eq. (8.5), if the system is composed of a single component ($y = 1$) the maximum number of phases equal to 3 is possible at $f = 0$, i.e., the system has zero degrees of freedom. Such a system is said to be *invariant*, meaning that it can exist, as has already been pointed out, only at strictly fixed values of temperature and pressure.

Let us approach the phase rule in the following way. To the equilibrium of any system at constant temperature and pressure there corresponds, as is known, a minimum of the Gibbs free energy, i.e.,

$$dG = 0$$

Suppose we have two phases, α and β, in contact, which contain a certain amount of components. Let a small amount dn_i of some component be transferred from phase α into phase β. If the Gibbs free energies are equal, respectively, to $G^{(\alpha)}$ and $G^{(\beta)}$, then the overall change in Gibbs free energy of the system is given by the relation

$$dG = -\left(\frac{\partial G^{(\alpha)}}{\partial n_i}\right)_{p,\,T,\,n_j \neq n_i} dn_i + \left(\frac{\partial G^{(\beta)}}{\partial n_i}\right)_{p,\,T,\,n_j \neq n_i} dn_i \tag{8.6}$$

According to the general equilibrium condition, dG is equal to zero at constants p and T. The derivatives dG/dn_i are actually the chemical potentials of the ith component in different phases. Therefore, Eq. (8.6) can be rewritten as follows:

$$\mu_i^{(\alpha)} = \mu_i^{(\beta)} \tag{8.7}$$

representing it as the equilibrium condition for a multicomponent and multiphase system*. As a matter of fact, since we may choose any component out of those making up the system and also take any pair of phases, the general equilibrium condition for a multicomponent and multiphase system will be the equality of the chemical potentials of all the components in all the phases.

Denoting the component by a subscript and the phase by a superscript, we may write, in extended form, the equilibrium condition for a system composed of y components and k phases:

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* In Chapter 5 when considering one-component systems we gave the equality of the molar Gibbs energies of a substance in two phases, $G_1 = G_2$ or $\mu_1 = \mu_2$, the subscripts indicating the phases.

$$\begin{array}{l} \mu_1^{(I)} = \mu_1^{(II)} = \ldots = \mu_1^{(k)} \\ \mu_2^{(I)} = \mu_2^{(II)} = \ldots = \mu_2^{(k)} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \mu_y^{(I)} = \mu_y^{(II)} = \ldots = \mu_y^{(k)} \end{array} \tag{8.8}$$

Here each row will contain $k - 1$ equations and the total number of equations in (8.8) will be $(k - 1)\, y$.

In order to define the state of the system it is necessary to specify its intensive properties or basic thermodynamic variables, the other parameters being functions of these variables. The important properties are primarily the pressure and temperature which are the same in all the phases in an equilibrium system (two variables). Besides, in the case of a multicomponent system the quantities that describe the state of the system are the concentrations of the components, say their mole fractions N_i. In view of the known equality, $\sum N_i = 1$, each of the phases will contain $y - 1$ independent concentrations. The total number of independent variables in k phases will thus be

$$(y - 1)\, k + 2 \tag{8.9}$$

The values of these variables are to be determined. Algebraically, the number of variables may either be equal to the number of equations or exceed it. If these numbers are equal, the system of equations is solved uniquely. All the variables are assigned a strictly fixed value, and the thermodynamic system is said to be invariant. But if the number of variables is larger, the difference between the number of variables and the number of equations, i.e.,

$$f = (y - 1)\, k + 2 - (k - 1)\, y = y + 2 - k \tag{8.10}$$

will express the number of independent variables, which may be assigned arbitrary values. These possibilities correspond to the number of degrees of freedom, and relation (8.10) is thus the Gibbs phase rule.

8.2. One-Component Systems

We shall now focus our attention once more on some one-component systems. Figure 8.3 shows the projection of the phase diagram of carbon on the p-T plane (after Bundy*). According to this author, there exist three crystalline modifications of carbon: graphite, diamond, and a special closest-packed metallic modification, which is stable at pressures higher than 600 kbars. The last modification can be judged about from indirect data, the existence of this modification being hypothetical. The diagram in Fig. 8.3 gives the following curves: *a*—the temperature dependence of the equilibrium pressure in the system graphite ⇌ diamond; *b*—the melting point of graphite versus the pressure; and *d*—the melting point of diamond versus the pressure. The curves *b* and *e* represent the extrapolation of the melting-point curves to the regions, which are unstable for the liquid. In accordance with this, the diamond region, for example, is divided by the curve *b* into two parts; part III is the region of existence of diamond and metastable graphite, and part IV which lies higher than the hypothetical curve is the diamond region proper. Accordingly, the part of the diagram marked by I is the graphite and metastable diamond region. The graphite region proper (it is not marked) lies between the curves *e* and *b*. There are two triple points on the diagram:

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* Bundy, F. P., *Science*, 137, 1067 (1962).

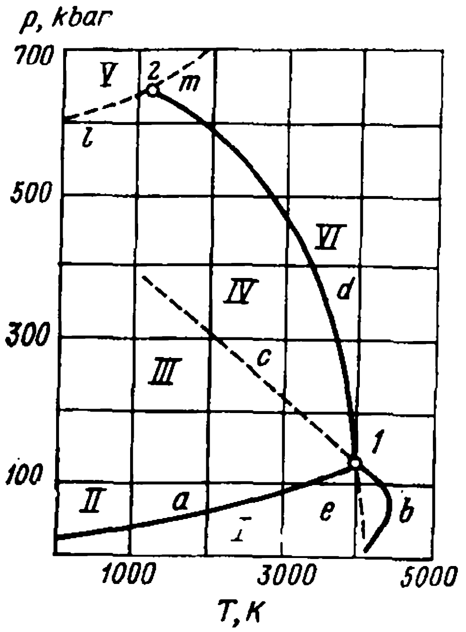

Fig. 8.3. Phase diagram for carbon after Bundy:

I—graphite and metastable diamond; *II*—the catalytic region studied; *III*—diamond and metastable graphite; *IV*—diamond; *V*—the most closely packed metallic modification of carbon (hypothetical); *VI*—liquid carbon; the coordinates of the triple point (*1*)—T = 3800-4000°K, p = 120-125 kbar (1 bar = 750.062 mm Hg = 0.986923 atm).

(a) the point *1*

$$\begin{tikzcd}
\text{graphite} \arrow[r, shift left] \arrow[d, shift left] & \text{diamond} \arrow[l, shift left] \arrow[d, shift left] \\
\text{liquid} \arrow[u, shift left] & \text{carbon} \arrow[u, shift left]
\end{tikzcd}$$

(b) the point *2*

$$\begin{tikzcd}
\text{closest-packed metallic modification} \arrow[r, shift left] \arrow[d, shift left] & \text{diamond} \arrow[l, shift left] \arrow[dl, shift left] \\
\text{liquid carbon} \arrow[u, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

which correspond to invariant systems. The part of the diagram marked by II may be called the catalytic region, the region where the conversion of graphite to diamond has been investigated in the presence of catalysts (certain metals have been used as catalysts).

Whereas the phase diagram of carbon refers to superhigh pressures and very high temperatures, the diagram given in Fig. 8.4 describes the properties of helium and, in the first place, of the isotope ^{4}He at very low temperatures. Inspection of this diagram should be started with the curve I, which expresses the temperature dependence of the saturated vapour pressure of liquid helium. Even here the following special feature of the phase diagram for helium can be distinguished: the vapour region does not contact the solid region.

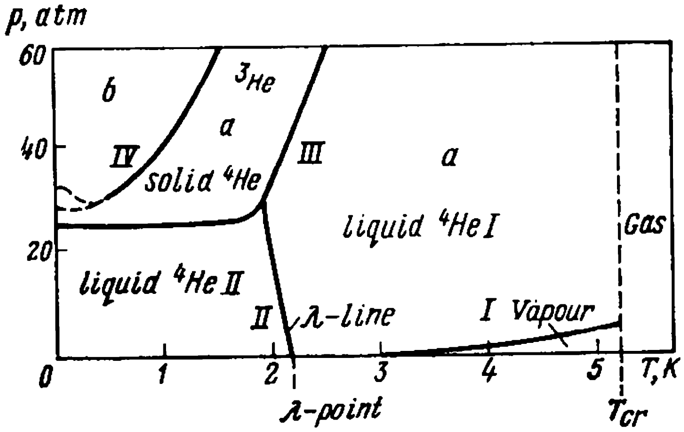

Fig. 8.4. Phase diagrams for helium:

a—isotope ^{4}He; curves: *I*—liquid ^{4}He I $\rightleftharpoons$ vapour; *II*—liquid ^{4}He I $\rightleftharpoons$ liquid ^{4}He II; *III*—^{4}He I $\rightleftharpoons$ solid ^{4}He; *b*—isotope ^{3}He; curve *IV*—liquid ^{3}He $\rightleftharpoons$ solid ^{3}He.

The most widespread helium isotope ^{4}He has a critical temperature of $T_c = 5.23°\text{K}$ at which the curve I stops. Liquid helium, to which this curve refers, is called helium I (He I). Upon cooling down to 2.18°K helium passes into another liquid state denoted by the symbol He II. This transition occurs without a heat effect but is accompanied by a change in the heat capacity; it belongs to the category of phase transitions of the second kind (second-order transitions) mentioned in Chapter 5. The point of the transition He I $\rightleftharpoons$ He II is called the lambda point (the λ-point)*. Liquid helium II exhibits unusual properties. For example, its viscosity is extremely low—this unique property is known as the superfluidity since helium passes almost instantaneously through small openings as if caving into them. The viscosity of He II is lower by 10^{-9} than the viscosity of water. It also displays heat superconductivity, which exceeds the heat conductivity of silver by about 100 times.

The liquid state of helium at not high pressures is retained down to the absolute zero, but, in spite of this, its entropy tends to zero at $T \to 0$. The change in the entropy of helium-4 as a function of temperature is given in Fig. 8.5. What attracts attention here is the absence of a discontinuity in entropy at the lambda point—a discontinuity characteristic of first-order phase transitions. What has been said can be confirmed by the following argument. According to one of the forms of the Clausius-Clapeyron equation:

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* It is so called because the corresponding curve somewhat resembles a written Greek letter λ.—*Tr.*

$$\frac{dp}{dT}=\frac{\underline{S}_{\text{liq}}-\underline{S}_{\text{sld}}}{\underline{v}_{\text{liq}}-\underline{v}_{\text{sld}}}$$

The densities of liquid and solid helium are different so that Δv is finite. The horizontal path of the melting-point curve (Fig. 8.4, curve III), however, shows that $dp/dT = 0$. Hence, we arrive at the conclusion that $\Delta \underline{S} = 0$, i.e., taking into account the third law, $S_{0(\text{liq})}$ is equal to zero. The rare helium isotope ^{3}He, which has recently become more available owing to the artificial preparation, also remains liquid at very low temperatures. While the isotope ^{4}He has no nuclear spin, the helium isotope ^{3}He has a nuclear spin equal to 1/2, and to this isotope there should be assigned at ordinary temperature a nuclear component of entropy, which is a consequence of two possible spin orientations, namely, $R \ln 2 = 1.38$ cal/deg·mole. At the lowest temperatures at which liquid ^{3}He has been studied (ca. 0.1°K) its entropy is only about 0.3 cal/deg·mole. Thus, the most of nuclear entropy is found to be lost under these conditions. The isotope ^{3}He in the liquid state does not display the properties of superfluidity and superconductivity.

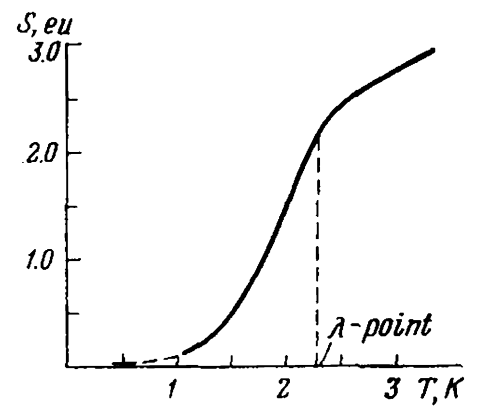


Fig. 8.5. The entropy of liquid helium near absolute zero.

The two helium isotopes can be prepared in the solid state by increasing the pressure up to 25-30 atm at 0.5°K. From the phase diagram in Fig. 8.4 it is seen that the equilibrium pressure for the system solid $\rightleftharpoons$ liquid in the case of ^{4}He remains nearly constant down to 2°K and then sharply increases. For ^{3}He the equilibrium pressure increases at temperatures exceeding 0.5°K.

In Chapter 6 (Sec. 6.13) we mentioned the special type of degeneracy of a system which manifests itself at low temperatures; it does so the more readily the smaller the mass of the molecules. Mention was also made of helium (^{4}He), for which only this type of degeneracy manifests itself distinctly in the special properties of liquid helium-4 which are demonstrated by the phase diagram (see Figs. 8.4 and 8.5).

8.3. Crystallization Diagrams for Two-Component Systems

Let us now turn to two-component systems; in order to describe the state of such systems it is necessary to specify three variables: for example, the pressure, temperature and concentration. The interplay of the three variables is depicted with the aid of a three-dimensional figure. Let us consider an example of such a figure for a binary system, whose components in the liquid state form homogeneous solutions throughout the complete range of concentrations; in the solid state they do not dissolve at all in one another (Fig. 8.6). Figure 8.6 shows the regions of the three states of aggregation: vapour, liquid and solid. The points *1*, *2*, and *1'*, *2'* correspond to the boiling points of the pure components at different pressures, and the points *5*, *6* and *5'*, *6'*, which lie below, correspond to the melting points. A number of surfaces can be distinguished on the diagram. Thus, the convex surface *132-1'3'2'* expresses the dependence of the boiling points of liquid solutions on the vapour com-

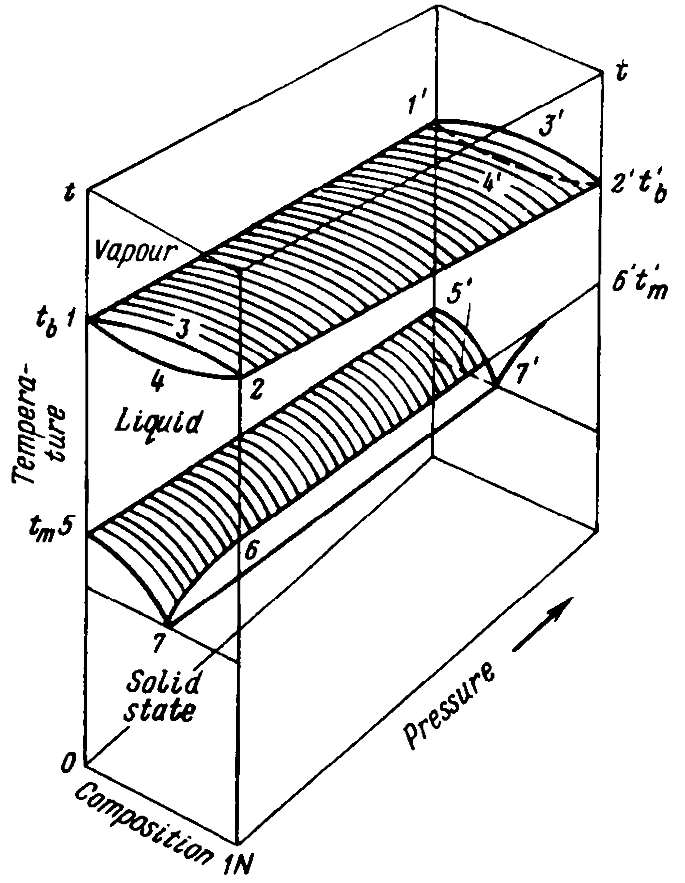


Fig. 8.6. Three-dimensional phase diagram for a binary system of substances, which are completely soluble in the liquid state and insoluble in the solid state: The points *1*, *2* and *1'*, *2'* are the boiling points of the components at various pressures; the points *5*, *6* and *5'*, *6'* are the melting points of the components.

position. Below is the concave surface *142-1'4'2'* which depicts the dependence of the boiling point on the composition of the liquid solution. Intersections of diagrams of this type were considered in Chapter 7 (see Fig. 7.10). The surface *576-5'7'6'* is the melting-point diagram, i.e., the dependence of the temperature at which the melt begins to crystallize on the melt composition and the pressure. To put it more exactly, at the temperatures and compositions corresponding to the points on the surface *57-5'7'* the liquid melt may be in equilibrium with the first solid component and, accordingly, with the second solid component on the surface *76-7'6'*.

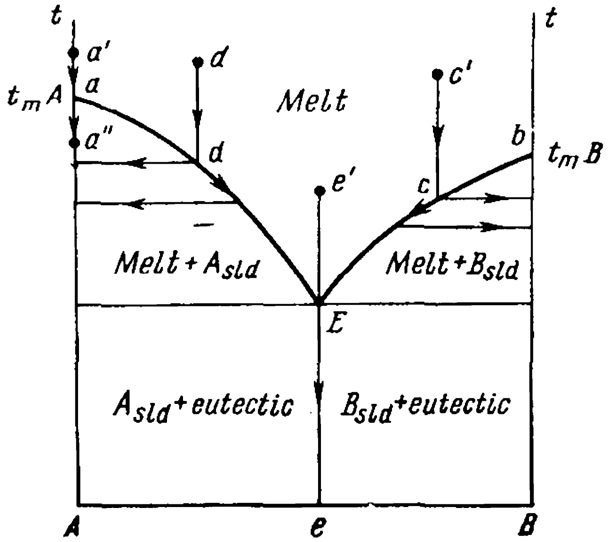


Fig. 8.7. Plane phase diagram (p = const) for substances which are completely soluble in one another in the liquid state and which do not form solid solutions (diagram of type I, which is given by the systems: Pb-Ag; Cd-Bi; Au-Tl; KCl-LiCl; CaO-MgO, etc.).

Usually, instead of complete diagrams of the type just described, one considers their cross sections at constant pressure. Second, since equilibria of the type liquid $\rightleftarrows$ vapour have already been examined (see Chapter 7), we shall confine ourselves to considering some melting-point diagrams.

If the pressure is assumed to be constant, the phase rule should be applied in a form different from Eq. (8.10):

$$f_{\text{cond}} = y + 1 - k \quad (8.11)$$

where of the two variables common to systems, the pressure and temperature, only the temperature is left; f_{cond} is the conditional number of degrees of freedom of a system existing at constant pressure (usually, at $p = 1$ atm).

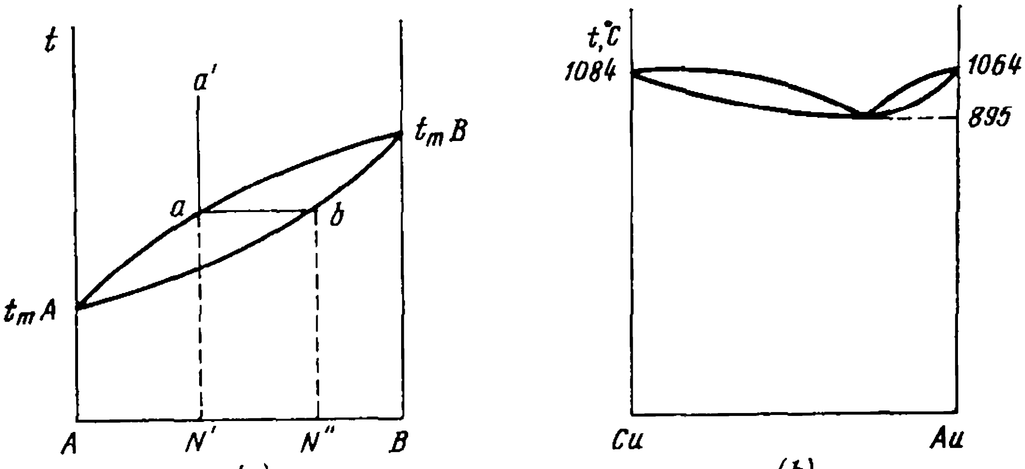
Let us consider in more detail a melting diagram of this type for a binary system, where the components dissolve in each other in the liquid state and do not dissolve in the solid state (Fig. 8.7). We start from the point a', which corresponds to the pure component A in the liquid state. Here the system has conditionally one degree of freedom—when heat is lost or gained, the temperature is changed, the number of phases remaining the same. If at the initial point a' the heat is lost by the system, its representative point moves downward in the direction of the point a at which the system is conditionally invariant. Here the liquid component A may be in equilibrium with A in the solid state. Therefore, for example, when the heat is evolved, the temperature will remain constant until all the liquid is crystallized. After this the loss of heat will be associated with a decrease in temperature and the representative point of the system will move towards *a″*, which means that the solid A is cooled.

If to the liquid component is added component B soluble in it, the temperature at which crystallization of such a melt starts will be lower than the melting-freezing point of pure component A. As we know from Chapter 7, this follows from Raoult's law. The curve *aE* reflects this decrease. The temperature of the onset of crystallization decreases also in those cases when component A is added to the liquid component B (the curve *bE*). The two curves intersect at point *E* called the *eutectic point*. In the region above the curves *aE* and *bE*—the melt region—the system has two degrees of freedom conditionally, i.e., here the temperature and composition can be changed arbitrarily and the number of phases (one phase) will remain constant.

If the system, whose state corresponds to the representative point *d′*, loses heat, then in moving downwards the state *d* is attained, where the melt is saturated with component A. Here the system becomes univariant, and further loss of heat leads to the separation of solid component A and to the movement of the representative point of the melt along the curve in the direction of the point *E*. Analogous phenomena, but associated with the separation of component B, occur also when the system loses heat, starting, for example, from the point *c′* in the right part of the diagram. At the eutectic point *E*, which can be attained from both sides, melt of composition *e* may be in equilibrium with the two solid components. Further loss of heat by the melt of this composition leads therefore to its crystallization at constant temperature with the formation of a solid eutectic consisting of a mixture of small crystals of A and B. Thus, the crystallization of systems of a composition to the left of the point *E* eventually yields crystals of A interspersed in the eutectic, and of those having a composition to the right of the point *E* yields crystals of B also interspersed in the eutectic. But if the melt has initially the eutectic composition *e*, then while losing heat it solidifies at constant temperature, forming a single solid eutectic.

At point *E*, where three phases are in equilibrium, i.e., the liquid eutectic and the solid components A and B, the system is conditionally invariant. We assign diagrams of the kind considered above to type I. These diagrams refer to the systems lead-silver, cadmium-bismuth, gold-thallium, KCl-LiCl, CaO-MgO, etc.

Type II includes diagrams where the components A and B form solutions over the entire range of compositions both in the liquid and the solid state. This type includes the systems Co-Ni, Bi-Sb, Ag-Au, Fe-Ni, etc. Figure 8.8 shows the diagram of a system of this type. Here the upper curve expresses the dependence of the melting point on the composition of the liquid solution, and the lower curve represents the dependence of the melting point on the composition of the solid solution. Note the similarity between diagrams of this type and the dependences of the vapour pressure or boiling point of a liquid solution on the composition considered in Chapter 7 (see Fig. 7.9). If we start from the representative point *a′*, i.e., the melt of composition N', and remove heat, then at the point *a* the melt will become completely saturated with the solid solution (the point *b*) of composition N'' (with a large content of component B). Using the difference between the compositions of the equilibrium phases,



(a) (b)

Fig. 8.8. Phase diagram for substances which are completely soluble in one another both in the liquid and in the solid state:

a—diagram of type II; b—variant of type II diagram with a minimum melting temperature for the system copper-gold.

we can separate this type of system into components by fractional crystallization, the principles of which are similar to the fractional distillation considered in Chapter 7. Just as on the vapour pressure-composition or boiling point-composition curves, here too extrema can appear, which indicate a considerable deviation of the solution from ideal behaviour. Figure 8.8*b* gives the melting-point diagram for the copper-gold system, which has a minimum melting temperature lying at 895°C. It may also be recalled that metallic sodium and potassium form a system, which is liquid at room temperature—in this case too there is a minimum melting temperature. Such diagrams with extrema are also referred to type II since here the general feature—complete solubility in the solid state—is not violated.

Type III is an intermediate case—complete solubility in the liquid state and limited solubility in the solid state. Here the composition of saturated solid solutions depends, as a rule, on temperature. Figure 8.9 shows a diagram of type III. Examples of systems belonging to this type are: Cu-Ag, Pb-Sn, $NaNO_3$-KNO_3.

If we cool the system, whose state corresponds to point a', then at point a the melt becomes saturated with solid solution b, which begins to separate upon further loss of heat. Since the solid solution is richer in component A the melt becomes enriched in component B as the temperature decreases; the solid solution, which is in equilibrium with the melt, also becomes enriched in this component (compare points a and b with points c and d). When being cooled the melt will eventually attain a state corresponding to point E. Here it may be in equilibrium with two solid solutions of compositions e' and e'', which separate upon further loss of heat. The composition of the eutectic melt e and of the solutions in equilibrium with it is maintained constant during the entire course of the isothermal process of crystallization—in this case there are three phases and the system is invariant. However, after the entire system has solidified the equilibrium compositions of the solid solutions undergo change with decreasing temperature along the curves gh and $g'h'$.

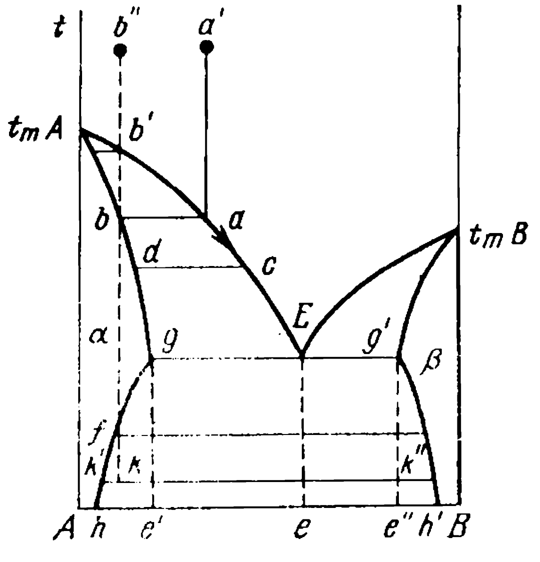


Fig. 8.9. Phase diagram of type III (the components show limited solubility in the solid state):

α – region of a homogeneous solid solution of B in A; β—region of a homogeneous solid solution of A in B.

A somewhat different picture is observed during the crystallization of melts that contain more of component A as compared with the composition e' of the solid solution, which is in equilibrium with the eutectic melt. Thus, when the melt b'' is cooled, its crystallization starts at point b'; in this case, as before, a solid solution is separated and the melt becomes enriched in component B. However, this continues until point a is reached, where the last traces of the melt are in equilibrium with solid solution of composition b, which coincides with composition b'' of the original system. In other words, in this case the crystallization eventually results in the formation of a single phase—a solid solution of composition b. This composition does not change upon further cooling, i.e., when the representative point moves up the vertical straight line bf through the region α of homogeneous solutions B and A. However, at point f the solid solution may be in equilibrium with the solution f'. Further decrease in temperature which corresponds, for example, to the movement of the representative system to point k must result in the formation of two phases—solid solutions k' and k''.

We shall now examine diagrams of type IV, which are associated with the formation of a sufficiently stable chemical compound composed of two components of composition A_nB_m (Fig. 8.10). This compound has a definite melting point $t_{m(A_nB_m)}$; it is said to have a *congruent* melting point. In this case, the compound behaves as an individual chemical substance and the melting diagram may be thought of as being composed of two diagrams of type I—one to the right and the other to the left of point *c*. The first diagram will refer to the chemical compound and component B, and the second to the same compound and component A. The point *c* is, so to say, the point of intersection of two curves since the slopes of the curves *cE′* and *cE″* at point *c* are substantially different. This is evidence of the complete stability of the compound, which melts without being dissociated. However, often at point *c* the melting point curve passes through a maximum, i.e., the curves *cE′* and *cE″* smoothly merge into each other, having zero slope. In such cases, the compound undergoes partial dissociation on melting.

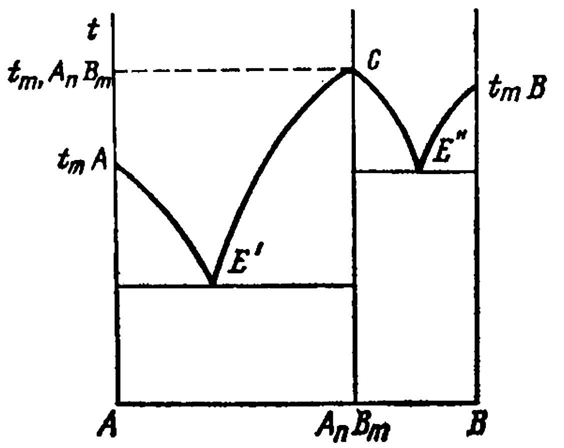


Fig. 8.10. Phase diagram of type IV.

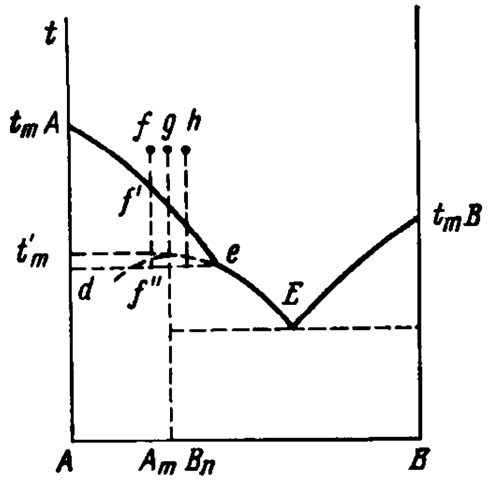


Fig. 8.11. Formation of a chemical compound A_mB_n with an incongruent melting point.

On the crystallization curve there is sometimes observed an inflection similar to the one shown in Fig. 8.11 (point *e*). Suppose this is a type V diagram. It is thought to be associated with the formation of an unstable chemical compound composed of two components and having composition A_mB_n. This compound decomposes at temperatures below its hypothetical melting point t'_m, i.e., the compound is said to have an *incongruent* melting point (or it is said to undergo a transition, or *peritectic reaction*, or *incongruent fusion*). As the melts, whose compositions lie in the region between the points *e* and *E*, are cooled, a chemical compound separates out; the subsequent events are the same as those taking place in the type I diagram (see Fig. 8.7). At the eutectic point the melt is in equilibrium with the solid compound and component B. The solid eutectic is also composed of solid A_mB_n and component B. Substantial differences from the previous case are observed upon crystallization of melts that contain a larger amount of component A than the composition corresponding to the point of inflection (the point *e*). For example, when the melt whose initial state corresponds to point *f* is cooled, first the component A begins to separate out at point *f'* and this continues until the system reaches the representative point *f''* on the straight line, where the melt becomes completely saturated with the chemical compound as well. Upon further loss of heat it is the chemical compound that begins separating out: it is formed by the interaction of the melt *e* with component A, which has separated out earlier. In the case under consideration, however, when the original melt contains more of component A than in the stoichiometric relation A_mB_n, part of solid A remains unused even after the entire melt has been used up for the formation of a solid chemical compound. Therefore, when the crystallization is complete, the system consists of component A and a chemical compound, i.e., of two phases. If the composition of the original melt is the same as the composition of the chemical compound A_mB_n (the starting point *g*), then the initially separated component A is completely consumed upon interaction with the melt which is also used up entirely for the formation of the solid chemical compound. The final result of crystallization is a one-phase system which contains only the chemical compound. Finally, if the initial composition of the melt corresponds to point *h*, then upon interaction of the initially separated A with the melt the latter remains in excess and, as a result, the compound A_mB_n and the eutectic will be crystallized. As examples of intermetallic compounds with congruent melting points may be cited $CdPb_2$ and Pd_3Pb, and of those undergoing incongruent fusion, PdPb and Pd_2Pb.

We have considered the simplest melting diagrams of two-component systems. They may be looked upon as the elements of more complicated cases, say when two components form several compounds. These cases will not be considered here and the reader is referred to special literature on the phase rule.

8.4. Three-Component Systems

In this section we shall mainly be concerned with the method of graphical representation of three-component systems with the aid of Gibbs or Roozeboom triangles. Both these authors make use of the properties of an equilateral triangle. Namely, Gibbs assumes each apex of the triangle to be equal to unity (or 100 per cent), taking into account that the sum of the vertical heights of a point from the three edges is equal to the height of the triangle. According to Roozeboom the edge of the triangle is taken as unity (or 100 per cent). If we draw through a given point on the interior of the triangle lines parallel to the sides, then the sum of the parallel distances from the interior point to the points of intersection with the sides, is equal to the side of the triangle.

In both methods, the apex of the triangle corresponds to a pure component: 100 per cent A, 100 per cent B, and 100 per cent C. The points on the side of the triangle represent the composition of a binary system. The points on the interior of the triangle represent the composition of a ternary system. According to Gibbs (Fig. 8.12) the content of a given component at point D (for example, component A) is determined by the segment of the perpendicular line Da drawn to the side opposite the apex A. According to Roozeboom, by drawing through D lines parallel to the sides one calculates the composition from the lengths of the segments a, b and c on any side (Fig. 8.12*b*). Using the equilateral triangle method, one must take into account the following property of the triangular graph—the straight line drawn from the apex to the side corresponds to systems with an invariable ratio of two components (Fig. 8.13). If component B is added to the mixture A-C of composition x, then the representative point of the system will be shifted to x'. It is clear that at points x and x' the ratios a/c and a'/c' are equal.

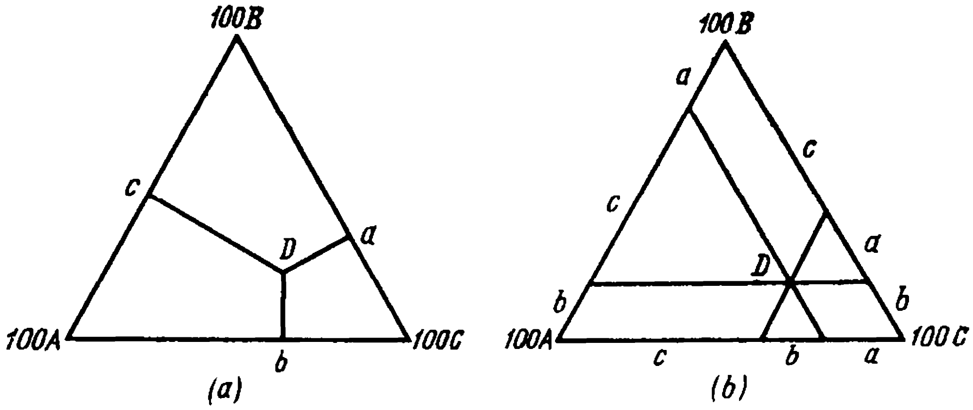


Fig. 8.12. Gibbs (*a*) and Roozeboom (*b*) triangles.

In studying the behaviour of a ternary system as a function of a variable other than the composition, say the temperature, it is marked off on the vertical axis. The system of coordinates will form a regular prism (Fig. 8.14), each section of which, being parallel to the base, will represent a constant-temperature surface (or a surface of any other quantity).

Let us now consider some diagrams that are obtained in studying ternary systems. Let us take, as an example, three liquids, two of which are partially soluble in each other and the other two pairs are completely miscible. In a particular case, these may be chloroform, water, and acetic acid. Figure 8.15*a* shows the diagram of a system in which the components A and B are partially soluble in each other, but above the temperature t_c (the critical solution temperature of A and B) these components are also miscible in all proportions. The heterogeneous region where the ternary system separates into two layers is represented by a three-dimensional figure *akba'b'k'*. The curve *aKb* limits the heterogeneous region in the binary system A-B, depending on temperature, and the curves *akb* and *a'k'b'* are the intersections of the ternary heterogeneous region with surfaces of the same temperature. If such intersections are drawn through a series of equal-temperature intervals and the resulting intersections are projected onto the base of a pyramid, a picture will be obtained which is similar to that shown in Fig. 8.15*b*, where the curves refer to different temperatures. If we introduce appropriate notations, then we can judge about the dependence of the partial miscibility on temperature from Fig. 8.15*b*.

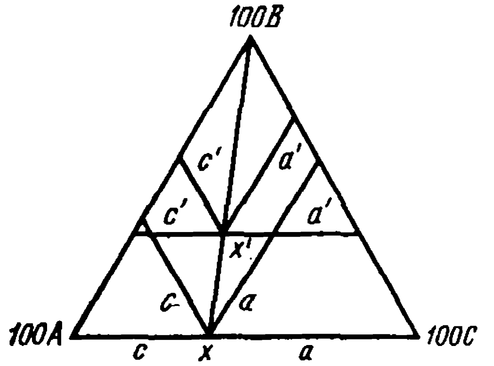


Fig. 8.13. Three-component systems.

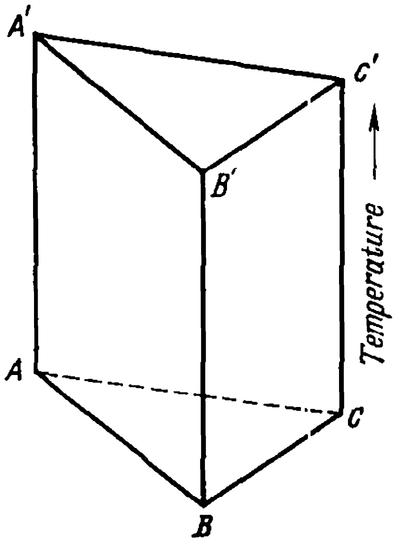


Fig. 8.14. A prismatic figure (a coordinate system) used for the study of ternary systems:
Two triangles *ABC* correspond to systems examined at various temperatures

In the case under consideration the system has no triple consolute temperature since the point *K* lies on the plane *AB*, where component C is absent. In the other cases the three-dimensional figure is helmet-shaped and its apex is inside the pyramid and corresponds to the triple critical solubility point. An example of a system giving such a helmet- or a dome-shaped boundary surface is phenol, water and acetone. The difference between the cases under consideration can be better understood if one compares Fig. 8.15*b* with Fig. 8.16, which gives the projections of the dome-shaped surface.

In some cases three liquids can give three pairs of partially miscible components. Such are, for example, water, ether and nitrile succinate. In this case, the isotherm may have the shape shown in Fig. 8.17*a* and *b*, where one can see three regions of two-phase heterogeneous mixtures. When the temperature is changed (more frequently, with a decrease in temperature) these regions may extend towards the central part of the triangle and overlap each other, as shown in Fig. 8.17*b*. Here homogeneous solutions are formed only with the compositions of the systems corresponding to the points of the light, unshaded portions. The portions marked x_1, x_2 and x_3 limit the regions of coexistence of two phases—the lighter and the heavier layer. Finally, a system whose composition corresponds to the points on the interior of the filled triangle *abc*, forms three layers, i.e., three liquid phases, which may, generally speaking, be in equilibrium with a fourth, vapour phase.* Thus, the number of degrees of freedom of the system will be equal to

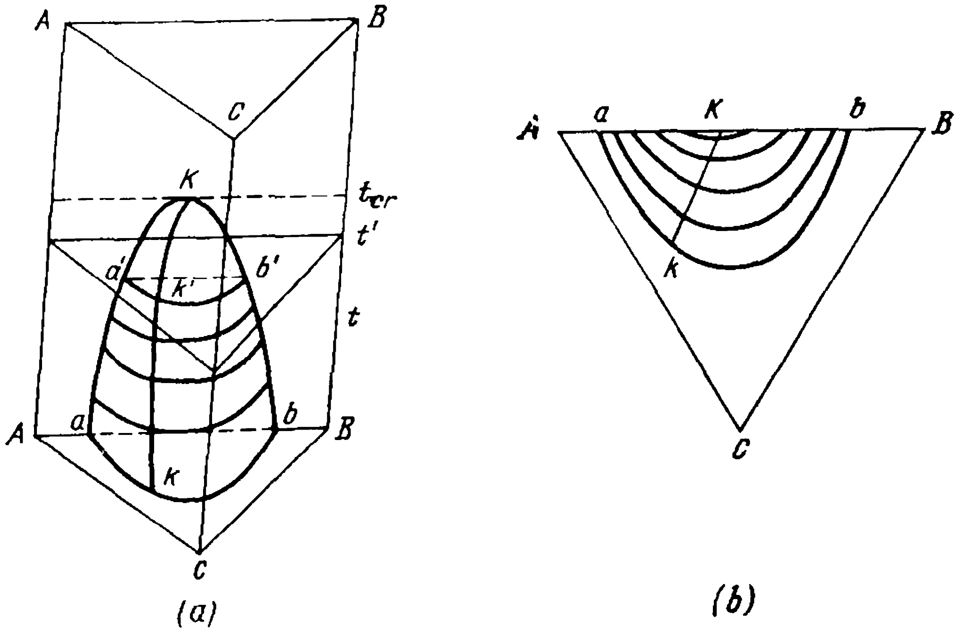


Fig. 8.15. Three-dimensional representation of limited solubility in a ternary system (*a*) (A and B show limited solubility; A and C, B and C are miscible in all proportions); the projections of the intersection of the three-dimensional figure (*a*) by isothermal planes (*b*).

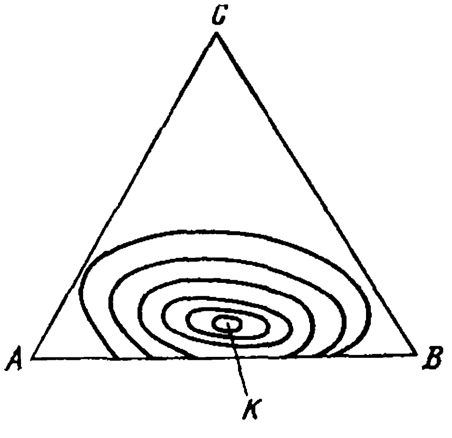


Fig. 8.16. The projections of the intersections of a cupola-shaped boundary surface of limited solubility: *K*—triple critical solubility point.

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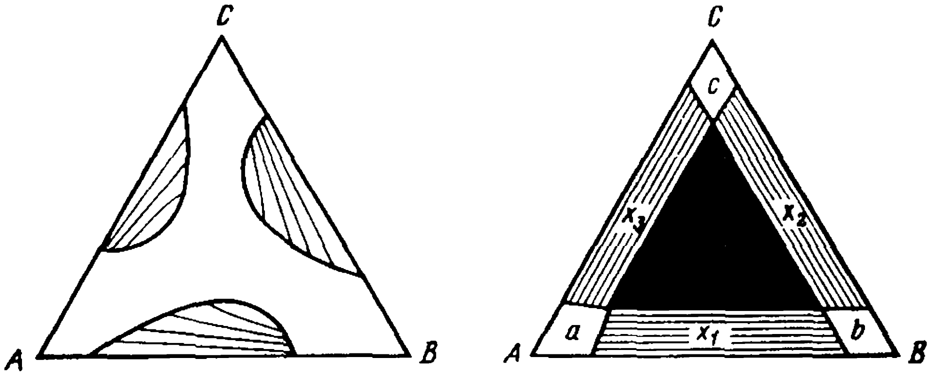
* This circumstance is not reflected in the diagram.

unity since

$$f = y + 2 - k = 3 + 2 - 4 = 1$$

If the temperature is fixed, the system will become conditionally invariant. This means that we have strictly definite compositions



(a) (b)

Fig. 8.17. Three liquids form three pairs of partially miscible components: *a—regions of two layers are outlined; b—x_1, x_2, x_3 are regions of two-phase systems; the triangle abc is the projection of a three-phase region.*

of three liquid layers corresponding to the points a, b and c. Naturally, the composition of the vapour phase will also be fixed.

In conclusion, let us consider the fusion diagram of a three-component system in which three pairs of components form planar diagrams of type I. Recall that this corresponds to complete miscibility in the liquid state and to the complete immiscibility in the solid state. The melting points of pure components are marked on the edges of the prism by the letters A, B, and C (Fig. 8.18). The faces of the prism give the solidification curves of binary systems—these are the curves Ae_1B, Ce_2A and Ce_3B. The points e_1, e_2 and e_3 are double eutectic points. The liquid system represented by the point e_1 may exist in equilibrium with solid components A and B. When certain amounts of component C are added to such a system, the temperature of the coexistence of liquid melt and components A

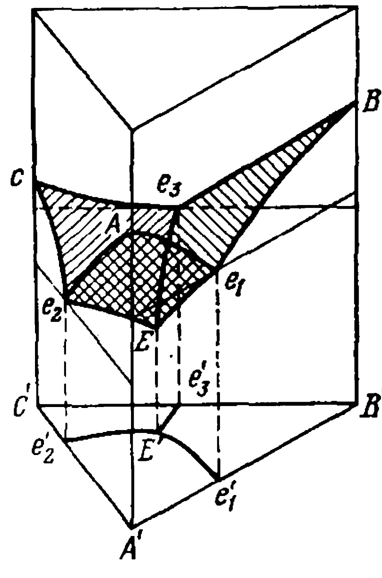


Fig. 8.18. Phase diagram for a three-component system (the components A, B, and C are completely miscible in the liquid state and do not form solid solutions):

e_1, e_2, e_3 are binary eutectic points; E is a triple eutectic point.

and B decreases—the corresponding curve e_1E is directed inside the prism and downwards. In other words, the points on the eutectic curve e_1E represent the composition of a three-component liquid mixture at equilibrium with components A and B. Analogous eutectic curves originate at points e_2 and e_3. Thus, the point on each of the eutectic curves e_1E, e_2E and e_3E represents the composition and temperature of systems that are in equilibrium with pairs of components A and B, C and A, and C and B, respectively. Here the system has one conditional degree of freedom (the pressure is constant). A loss of heat leads to the crystallization of a binary eutectic, a decrease in temperature and to the enrichment of the melt with the component of the "opposite edge". Thus, a system whose representative point moves downward along the eutectic curve e_1E gives the eutectic A-B and becomes enriched in component C. One should also remember that the surfaces, whose intersections produce the curves e_1E, e_2E, and e_3E, constitute the locus of the points of ternary melts, which are in equilibrium with one of the solid components. Here the systems have conditionally two degrees of freedom. Finally, the intersection of three binary eutectic curves forms a triple eutectic point E at which ternary melt is simultaneously in equilibrium with three solid components. Here the system is conditionally invariant, i.e., at a given pressure it exists at a strictly fixed composition and temperature. A diagram of this type is given, for example, by bismuth, lead, and tin. Their melting points are approximately equal to 268, 325, and 232°C, respectively, and the triple eutectic point lies at 96°C.

The ternary system that has been considered above belongs to the category of the simplest systems. The picture can be considerably complicated by the formation of chemical compounds and the appearance of partial miscibility. For such more complicated cases the reader is referred to specialized literature; here the principal objective has been to acquaint the reader with the general principles and main types of phase diagrams.

Chapter 9

Application of Thermodynamics to Non-Equilibrium (Irreversible) Processes

1. INTRODUCTION. METHODS AND DISCONTINUOUS SYSTEMS

The beginning of the development of the thermodynamics of nonequilibrium (irreversible) processes (or simply nonequilibrium or irreversible thermodynamics) should be dated back to Clausius, who introduced the concept of the *uncompensated heat* (1850), which is, in essence, basic to this field of thermodynamics. However, it was William Thomson (Lord Kelvin) who was actually the first to apply thermodynamic relationships to the study of nonequilibrium processes (1854). At a much later time a large contribution to the further progress of nonequilibrium (irreversible) thermodynamics was made by de Donder. His principal idea was that one could go beyond the mere statement of the inequality in the formulation of the second law and give an exact quantitative definition of the *entropy production.* In 1922 de Donder established the relationship between the Clausius uncompensated heat and the chemical affinity. In 1931 Onsager formulated his famous *reciprocal relations* which form the basis for the study of relationships among the various nonequilibrium processes in the so-called linear region. The subsequent development of nonequilibrium thermodynamics and the substantiation of its formalism is associated with the names of Prigogine, Glandsdorf, Casimir, and others. Thus, in the works of I. Prigogine* the methods of nonequilibrium thermodynamics were extended to the region where the relations between fluxes and forces are no longer linear.

Two objectives are pursued in this chapter. First, to acquaint the reader with the elements of the general theoretical foundations of nonequilibrium thermodynamics without delving into practical applications. Second, to provide a brief survey of the modern status of the field of physics and physical chemistry under consideration, which in the author's opinion may only conditionally be called thermodynamics and is, in fact, a branch of physical (and partly chemical) kinetics.

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* I. Prigogine was awarded a Nobel Prize in 1977 for his work in the field of thermodynamics.

9.1. Basic Concepts and Definitions

As known, the usual formulation of the second law of thermodynamics has the form

$$dS = \frac{\delta Q}{T} \tag{9.1}$$

and

$$dS > \frac{\delta Q}{T} \tag{9.2}$$

The equality in (9.1) holds for equilibrium processes, which are studied in courses of ordinary thermodynamics. On the other hand, the inequality in (9.2) characterizes a spontaneous nonequilibrium process and is usually used only as a criterion of the directionality of spontaneous processes. For this second case, i.e., the inequality, Clausius proposed a different form of the second law:

$$dS - \frac{\delta Q}{T} \equiv \frac{\delta Q'}{T} \tag{9.3}$$

Clausius called the new quantity $\delta Q'$ (or dQ') the *uncompensated heat*. Perhaps, the term is not a particularly happy choice because this is not the heat actually absorbed or evolved by the system but rather the heat that could have been absorbed in an equilibrium (reversible) process in addition to a nonequilibrium quantity δQ in order to restore the equality (9.1). On the basis of (9.3) we can also write the second law in the following, more general form:

$$dS = \frac{\delta Q}{T} + \frac{\delta Q'}{T} \tag{9.4}$$

From the relations written above it must be clear that for equilibrium processes $\delta Q' = 0$ and for nonequilibrium (irreversible) processes

$$\delta Q' > 0 \tag{9.5}$$

In other words, the heat $\delta Q'$ is always positive and is produced within the system as a result of nonequilibrium processes leading to its irreversible change.

The physical significance of the uncompensated heat will be clearer if the total entropy change of the system is divided into two parts:

$$dS = d_eS + d_iS \tag{9.6}$$

where d_eS is the external entropy change and is associated with the equilibrium absorption of heat from the outside world; d_iS is the internal entropy change by irreversible changes taking place in the interior of the system. Comparing Eqs. (9.4) and (9.6), we can write:

$$d_eS = \frac{\delta Q}{T} \tag{9.7}$$

and

$$d_iS = \frac{\delta Q'}{T} \tag{9.8}$$

The last relation connects the uncompensated heat and the production of entropy (or the creation of entropy, d_iS) inside the system as a result of the irreversible processes that take place in it.

Relations (9.5) and (9.8) should be understood in the sense that any nonequilibrium process occurring in the system (for example, the mixing of gases, the spontaneous uncoiling of a compressed spring) increases the disorder of the molecular state of the system, leading to its greater randomness. Quantitatively, this manifests itself in an increase in the *thermodynamic probability* of the state of the system and, hence, its entropy. Thus, the uncompensated heat, the basic quantity in nonequilibrium thermodynamics, is equal, in accordance with Eq. (9.8), to the *entropy production* multiplied by the temperature ($\delta Q' = T\,d_iS$).

In contrast to reversible processes, nonequilibrium (irreversible) changes proceed at a finite rate; the study of these processes is, in fact, the concern of physical and chemical kinetics. It is for this reason that the time factor enters the scene, a factor which is dropped out of the consideration in ordinary equilibrium (reversible) thermodynamics. Thus, if the entropy d_iS is created during the time dt, then one speaks of the *rate of entropy production*:

$$\sigma = \frac{d_iS}{dt} \geqslant 0 \tag{9.9}$$

It is the calculation of σ values that will constitute our task in the subsequent discussion.

It should be added to what has been said above that for an isolated system (U = const, v = const) the total entropy change is equal to the internal change in entropy, i.e.,

$$dS_{U,v} = d_iS \geqslant 0 \tag{9.10}$$

9.2. The Uncompensated Heat and the Change of Thermodynamic Functions

The uncompensated heat may be related to the change of the well-known thermodynamic functions. One proceeds from the combined formula for the first and second laws of thermodynamics and also from relation (9.4):

$$\delta Q = dU + p\,dv = T\,dS - \delta Q' \tag{9.11}$$

It should be noted that the first law is used here in its simplest form, which is applicable to closed systems subjected only to the external forces, i.e., the forces of surface tension are considered to be negligibly small and no electric changing and magnetization are present, etc. Solving the second equality in (9.11) for the differential of the internal energy, we write down

$$dU = T\,dS - p\,dv - \delta Q' \tag{9.12}$$

and we become convinced that if the volume and entropy of the system are constant, then

$$dU_{S,\,v} = -\delta Q' \leqslant 0 \tag{9.13}$$

that is, to put it otherwise, in a system existing under the conditions indicated (S = const and v = const) the uncompensated heat equals a decrease in the internal energy. At the same time, according to the general criteria of spontaneity, which are also treated in general thermodynamics, this decrease is the criterion of the irreversibility of the process.

Further, differentiating the definition of the enthalpy $H = U + pv$ and substituting dU from Eq. (9.12), we obtain:

$$dH = T\,dS + v\,dp - \delta Q' \tag{9.14}$$

From this it follows that at constant entropy and pressure

$$dH_{S,\,p} = -\delta Q' \leqslant 0 \tag{9.15}$$

Hence, under these conditions (S = const and p = const) the uncompensated heat is equal to a decrease in the enthalpy. Quite analogously, if we proceed from the definitions of the Helmholtz and Gibbs free energies ($F = U - TS$ and $G = U - TS + pv$), we can write for constant temperature and volume:

$$dF_{T,\,v} = -\delta Q' \leqslant 0 \tag{9.16}$$

and for constant temperature and pressure:

$$dG_{T,\,p} = -\delta Q' \leqslant 0 \tag{9.17}$$

As will be shown further in the text, relations (9.16) and (9.17) allow one to relate the uncompensated heat to the chemical affinity of a chemical reaction which is considered in the next section.

9.3. The Chemical Variable, Chemical Affinity and the First Law

Let us write a chemical reaction in a general form:

$$\nu_1 B_1 + \nu_2 B_2 + \ldots \rightleftarrows \nu_1' B_1' + \nu_2' B_2' + \ldots \tag{9.18}$$

where ν_i are stoichiometric coefficients; B_i are the symbols for the participants in the reaction (the reactants and products). Suppose that the reaction has proceeded from left to right, so that the numbers of moles of substances B_i have been changed by dn_i. We define the change of a chemical variable by means of the relation

$$d\xi = \frac{dn_i}{\nu_i} \tag{9.19}$$

which is known as the *extent of reaction* or the *reaction coordinate.* If $\Delta\xi = 1$, *one equivalent of reaction* is said to have occurred.

In 1922 de Donder introduced the following definition of the chemical affinity A in terms of the Clausius uncompensated heat:

$$\delta Q' = \mathbf{A}\, d\xi \geqslant 0 \tag{9.20}$$

and here, as before, the equality holds for equilibrium and the inequality for the spontaneous, i.e., irreversible, course of the reaction. As a whole, relation (9.20) is called the *de Donder inequality.*

It can incidentally be shown that relation (9.20) does not contain many new aspects as compared with the classical definitions of the chemical affinity. Thus, using relation (9.17) and also the definition of the chemical potential of a substance γ in a mixture* according to Gibbs, $\mu_\gamma = (\partial G/\partial n_\gamma)_{T,\,p,\,n_\beta}$, we can write the following relationship:

$$\mathbf{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,\,p} = -\sum \nu_\gamma \mu_\gamma \tag{9.21}$$

At an earlier time (van't Hoff and Helmholtz) used, as a measure of the chemical affinity, let us say, at constant pressure and temperature, the maximum useful work corresponding to one equivalent of reaction ($\Delta\xi = 1$). This work is equal to a decrease in G, i.e., $-\Delta G_{T,p}$, which is found provided that the chemical potentials are held constant. The de Donder affinity differs from the classical affinity in nearly the same manner as the true rate (a derivative) differs from the average rate (the ratio of finite differences). What has just been said can be explained more fully as follows. The finite change in the Gibbs free energy in a chemical reaction means that $\Delta G = G_{\text{products}} - G_{\text{reactants}}$. But, on the other hand, the Gibbs free energy of a homogeneous system, in which a reaction takes place, can be expressed with the aid of Euler's theorem as follows: $G = \sum n_\gamma \mu_\gamma$. If a chemical reaction has occurred in the phase under consideration and the chemical variable has changed by $\Delta\xi = (n_\gamma - n_\gamma^\circ)/\nu_\gamma = 1$, the corresponding increase in the Gibbs free energy can be given in the following form:

$$\Delta G = \Big(\sum_\gamma n_\gamma \mu_\gamma\Big)_f - \Big(\sum_\gamma n_\gamma^\circ \mu_\gamma^\circ\Big)_i$$

Since the chemical potentials μ_γ do not necessarily have the same values in the initial and final states, it follows that $\Delta G \neq$

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* Here we have to change the subscript denoting the component since the letter i used stands for internal.

$\neq \sum \mu_\gamma (n_\gamma - n_\gamma^\circ)$ and, further, if we assume that $\Delta\xi = 1$, then $\Delta G \neq \sum \nu_\gamma \mu_\gamma$ or $\Delta G \neq -\mathbf{A}$. In other words, the finite difference ΔG and the de Donder affinity $\mathbf{A} = -\sum \nu_\gamma \mu_\gamma$ do not coincide, strictly speaking. More exactly, they will coincide if as the chemical reaction proceeds further the initial composition, temperature and pressure of the reacting system do not practically change. To illustrate, one can, for example, imagine a system, in which all the participants in the reaction are contained in large amounts (all the n_γ° are very great). If in such a system the reaction proceeds one equivalent, then the disappearance of ν_γ moles of the reactants and the appearance of ν_γ° moles of the products do not change the chemical potentials of the reactants and then the finite difference ΔG can really be expressed by the sum $\sum \nu_\gamma \mu_\gamma$, where μ_γ are the initial values of the chemical potentials. Nonetheless, the definition of the affinity given by de Donder, (9.21), is more rigorous than the classical definition.

Let us now write the first law for a system in which a chemical reaction is proceeding. We proceed from a simple formula: $\delta Q = dU + p\,dv$, which is applicable to systems subjected solely to the forces of external pressure (the surface tension is negligibly small and no electric charging and magnetization are present). We assume that the internal energy and volume of a multicomponent homogeneous system of a given initial composition are functions of three variables, as has already been done in Chapter 1:

$$U = U(T, p, \xi) \text{ and } v = v(T, p, \xi) \tag{9.22}$$

Thus, the total differentials

$$dU = \left(\frac{\partial U}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial U}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial U}{\partial \xi}\right)_{T,p} d\xi \tag{9.23}$$

and

$$dv = \left(\frac{\partial v}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial v}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial v}{\partial \xi}\right)_{T,p} d\xi$$

Further, substituting these differentials into the formula of the first law, we obtain:

$$\delta Q = \left[\left(\frac{\partial U}{\partial T}\right)_{p,\xi} + p\left(\frac{\partial v}{\partial T}\right)_{p,\xi}\right] dT + \left[\left(\frac{\partial U}{\partial p}\right)_{T,\xi} + p\left(\frac{\partial v}{\partial p}\right)_{T,\xi}\right] dp + \left[\left(\frac{\partial U}{\partial \xi}\right)_{T,p} + p\left(\frac{\partial v}{\partial \xi}\right)_{T,p}\right] d\xi \tag{9.24}$$

The coefficients for the differentials in (9.24) may be designated and termed as follows:

$$\left(\frac{\partial U}{\partial T}\right)_{p,\xi} + p\left(\frac{\partial v}{\partial T}\right)_{p,\xi} = C_{p,\xi}$$

is the heat capacity at constant pressure and composition.

$$\left(\frac{\partial U}{\partial p}\right)_{T,\xi}+p\left(\frac{\partial v}{\partial p}\right)_{T,\xi}=h_{T,\xi}$$

is the heat of the isothermal change of the pressure at constant composition; and

$$\left(\frac{\partial U}{\partial \xi}\right)_{T,p}+p\left(\frac{\partial v}{\partial \xi}\right)_{T,p}=h_{T,p}$$

is the differential heat of reaction at constant temperature and pressure.

Now the first law can be rewritten in terms of the *thermal coefficients* introduced:

$$\delta Q=C_{p,\xi}\,dT+h_{T,\xi}\,dp+h_{T,p}\,d\xi \tag{9.25}$$

The thermal coefficient $h_{T,p}$ includes the change in the internal energy due to a chemical reaction and also the work of expansion of the system, $p\,(\partial v/\partial\xi)_{T,p}$ (which is also associated with the reaction). The definition of the heat of reaction introduced here differs somewhat from the ordinary heat effect, $Q_{T,p}=\Delta H_{T,p}$, in that $h_{T,p}=(\partial H/\partial\xi)_{T,p}$, i.e., it is derivative, whereas $Q_{T,p}$ is the finite difference $\Delta H=H_{\text{products}}-H_{\text{reactants}}$.

This difference is the same as in the case of the de Donder and classical definitions of the affinity. However, in this particular case the difference is less significant.

9.4. The Chemical Variable and the Second Law. The Rate of Entropy Production

We shall assume that the entropy too is a function of three variables, $S=S\,(T,\,p,\,\xi)$ and

$$dS=\left(\frac{\partial S}{\partial T}\right)_{p,\xi}dT+\left(\frac{\partial S}{\partial p}\right)_{T,\xi}dp+\left(\frac{\partial S}{\partial \xi}\right)_{T,p}d\xi \tag{9.26}$$

Recall the Clausius equation (9.4), i.e., $\delta Q'=T\,dS-\delta Q$; substituting the differential of the entropy (9.26) and δQ from the first law (9.25) into it, we get:

$$\delta Q'=\left[T\left(\frac{\partial S}{\partial T}\right)_{p,\xi}-C_{p,\xi}\right]dT+\left[T\left(\frac{\partial S}{\partial p}\right)_{T,\xi}-h_{T,\xi}\right]dp+$$
$$+\left[T\left(\frac{\partial S}{\partial \xi}\right)_{T,p}-h_{T,p}\right]d\xi\geqslant 0 \tag{9.27}$$

But, as one can see, the coefficients in dT and dp are equal to zero, since the changes in T and p, for example, are arbitrary and independent, and $\delta Q'$ is always positive. Hence, the uncompensated heat in a system in which a chemical reaction is taking place, is defined by

$$\delta Q' = \left[T \left(\frac{\partial S}{\partial \xi} \right)_{T,\,p} - h_{T,\,p} \right] d\xi \geqslant 0 \tag{9.28}$$

But, taking cognizance of the de Donder definition (9.20), we obtain the following expression for the chemical affinity:

$$A = -h_{T,\,p} + T \left(\frac{\partial S}{\partial \xi} \right)_{T,\,p} \tag{9.29}$$

which is essentially the analogue of the Gibbs-Helmholtz equation.

Further, let us introduce the time factor and define the *rate of reaction throughout the entire system* according to de Donder (1937):

$$w_{T,\,p} = \frac{d\xi}{dt} \tag{9.30}$$

Now, on the basis of Eqs. (9.28), (9.29), and (9.30) we can write:

$$\frac{\delta Q'}{dt} = \mathbf{A} \frac{d\xi}{dt} = \mathbf{A} w \geqslant 0 \tag{9.31}$$

and deduce the following general conclusions concerning the affinity and the reaction rate:

$$\begin{array}{ll} \mathbf{A} > 0 & w \geqslant 0 \\ \mathbf{A} < 0 & w \leqslant 0 \\ \mathbf{A} = 0 & w = 0 \end{array}$$

The last case corresponds to the equilibrium state and cannot include the relation $\mathbf{A} = 0$, $w \neq 0$, i.e., the finite rate at equilibrium. On the other hand, $w = 0$ at $\mathbf{A} \neq 0$ in the first two cases implies the kinetically frozen reaction.*

From relation (9.31), taking account of the relationship between the uncompensated heat and the entropy production (9.8), we can write:

$$T \frac{d_i S}{dt} = T\sigma_{\text{ch}} = \mathbf{A} w \geqslant 0 \tag{9.32}$$

where σ_{ch} [see Eq. (9.9)] is the rate of entropy production in the system. The subscript "ch" indicates the nature of the cause of the entropy production—in this case the only nonequilibrium (irreversible) process that takes place is a chemical reaction. Expression (9.32) has a form which is generally characteristic of the thermodynamics of nonequilibrium (irreversible) processes, namely, the rate of entropy production multiplied by the absolute temperature ($T\sigma$) is equal to the product of a certain generalized force (**A**) by the generalized flux (w) caused by this force.

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* For example, a mixture of hydrogen and oxygen does not react at room temperature in the absence of a catalyst, though $\mathbf{A} \gg 0$.

9.5. The Rate of Entropy Production in Heat Transfer

As a further example of irreversible processes, let us consider a heat transfer process. Imagine two homogeneous closed* systems at different temperatures T^{I} and T^{II}. The systems are separated from each other by a diathermal wall of area Ω. The heat can readily flow through it into the system or can be supplied from the surroundings. Let the total amounts of heat received by the systems I and II for the time dt be equal to $\delta^{\mathrm{I}}Q$ and $\delta^{\mathrm{II}}Q$. We can write the entropy change for the two systems:

$$dS = dS^{\mathrm{I}} + dS^{\mathrm{II}} = \frac{\delta^{\mathrm{I}}Q}{T^{I}} + \frac{\delta^{\mathrm{II}}Q}{T^{\mathrm{II}}} \tag{9.33}$$

The amounts of heat passing through the diathermal wall are denoted as $\delta_i^{\mathrm{II}}Q = -\delta_i^{\mathrm{I}}Q$ since these amounts are equal by absolute value and opposite in sign. In general, we can write:

$$\begin{aligned} \delta^{\mathrm{I}}Q &= \delta_i^{\mathrm{I}}Q + \delta_e^{\mathrm{I}}Q \\ \delta^{II}Q &= \delta_i^{II}Q + \delta_e^{II}Q \end{aligned} \tag{9.34}$$

Here, as before, the subscript "e" signifies that the amount of heat is received from the environment. Thus, from Eqs. (9.33) and (9.34) we obtain:

$$dS = \frac{\delta_e^{\mathrm{I}}Q}{T^{\mathrm{I}}} + \frac{\delta_e^{\mathrm{II}}Q}{T^{\mathrm{II}}} + \delta_i^{\mathrm{II}}Q\left[\frac{1}{T^{\mathrm{II}}} - \frac{1}{T^{\mathrm{I}}}\right] = d_eS + d_iS \tag{9.35}$$

But we are interested here in what takes place in the interior of the complex system (I + II), i.e., in the second part of relation (9.35) associated with heat transfer. On the basis of the second law in the form (9.8) we can write:

$$d_iS = \delta_i^{\mathrm{II}}Q\left[\frac{1}{T^{\mathrm{II}}} - \frac{1}{T^{\mathrm{I}}}\right] \geqslant 0$$

This means that $\delta_i^{\mathrm{II}}Q > 0$ and the heat flux is directed from I to II provided that $T^{\mathrm{I}} > T^{\mathrm{II}}$. The production of entropy is evidently discontinued (the system is brought to a state of thermal equilibrium) when $T^{\mathrm{II}} = T^{\mathrm{I}}$.

This is the case with a system having a diathermal wall—a well-defined boundary surface. If the system is continuous but has a temperature field, the difference $1/T^{\mathrm{II}} - 1/T^{\mathrm{I}}$ should be replaced by a vectorial quantity—the change in $1/T$ by unit length along the normal to the isothermal surfaces $d\,(1/T)/dn$, i.e., by the gradient

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* In contrast to an open system, a closed system cannot exchange matter with the surroundings.

$(1/T)$ [grad $(1/T)$]. Thus, for a continuous system we write an expression for the entropy production in the following form:

$$d_iS = \delta_iQ \cdot \mathrm{grad}\,\frac{1}{T}$$

Then we divide by dt and Ω, which is the cross-sectional area of the system across the temperature gradient:

$$\sigma_{\mathrm{therm}} = \frac{d_iS}{\Omega\,dt} = \frac{\delta_iQ}{\Omega\,dt}\,\mathrm{grad}\,\frac{1}{T} = W\,\mathrm{grad}\,\frac{1}{T} \tag{9.36}$$

We have obtained a relation which expresses the rate of the entropy production per unit volume due to the heat flux W, i.e., the amount of heat that passes per unit time through the unit surface area of the isothermal cross-section of the system.

From dimensionality considerations and for the effects of various fluxes to be summed up further, we rearrange Eq. (9.36) and obtain an expression for $T\sigma_{\mathrm{therm}}$. To this end, we make use of the identity

$$\mathrm{grad}\,\frac{1}{T} = -\frac{\mathrm{grad}\,T}{T^2}$$

and write, instead of Eq. (9.36),

$$T\sigma_{\mathrm{therm}} = \left(-\frac{\mathrm{grad}\,T}{T}\right)W \tag{9.37}$$

Here, again as in the case of Eq. (9.32), the rate of entropy production multiplied by T is represented in the form of two cofactors—the heat flux W and the quantity $-\mathrm{grad}\,T/T$, which should be called the thermal force or the thermal affinity. The thermal force causes the flow of heat, i.e., an irreversible (nonequilibrium) process leading to the creation of entropy.

We shall emphasize once again that the basic concept of the thermodynamics of irreversible phenomena is the rate of production of entropy σ. In its turn, the rate of entropy production times the temperature is equal to $\delta Q'/dt$, i.e., the rate of appearance in the system of the Clausius uncompensated heat. However, in view of the vagueness of the physical significance of $\delta Q'$, this concept will not be used in the subsequent discussion.

9.6. Open Systems. The First Law of Thermodynamics

We shall now be concerned with open systems, i.e., systems which are capable of exchanging both energy and material with the surroundings.

The first law of thermodynamics, which has the form $dU = \delta Q - p\,dv$ for closed systems subjected only to the external pressure, is written in the following form for an open system:

$$dU = d\Phi - p\,dv \tag{9.38}$$

where $d\Phi$ is the energy flux (or, more exactly, the enthalpy flux) received by the system in time dt as a result of heat transfer and together with the material being transported—the enthalpy of the substance. For an open system $p\,dv$ does not necessarily correspond to the actual work, since the volume may undergo change because of the substance being transported by convection or by any other way.

Instead of Eq. (9.38), we can write the total enthalpy change as

$$dH = d\Phi + v\,dp \tag{9.39}$$

Let us now consider a complex system, i.e., two systems I and II which are separated by a real or imaginary boundary surface Ω. The total energy flux $d^{\mathrm{I}}\Phi$ received by system I during the time dt is equal to the flow across the boundary surface Ω, i.e., $d_i^{\mathrm{I}}\Phi$ plus the flux $d_e^{\mathrm{I}}\Phi$ supplied from the surroundings. For the sake of simplicity, we shall assume the pressures p^{I} and p^{II} to be identical and equal to p. Then the first law (9.38) may be written, first, for systems I and II separately:

$$d_i^{\mathrm{I}}\Phi + d_e^{\mathrm{I}}\Phi = dU^{\mathrm{I}} + p\,dv^{\mathrm{I}} \quad \text{and} \quad d_i^{\mathrm{II}}\Phi + d_e^{\mathrm{II}}\Phi = dU^{\mathrm{II}} + p\,dv^{\mathrm{II}}$$

and, second, for the entire complex system (I + II):

$$d_e^{\mathrm{I}}\Phi + d_e^{\mathrm{II}}\Phi = d\,(U^{\mathrm{I}} + U^{\mathrm{II}}) + p\,(dv^{\mathrm{I}} + dv^{\mathrm{II}}) \tag{9.40}$$

From this it follows that

$$d_i^{\mathrm{II}}\Phi = -d_i^{\mathrm{I}}\Phi \tag{9.41}$$

that is, the energy flux received by system I from system II is equal in absolute magnitude but opposite in sign to the energy flux from I to II.

Assuming the enthalpy of the system to be a function of the temperature, pressure and the number of moles of its components, i.e., $H = H\,(T,\ p,\ n_\gamma)$, we write the total differential:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,\,n_\gamma} dT + \left(\frac{\partial H}{\partial p}\right)_{T,\,n_\gamma} dp + \sum_\gamma \left(\frac{\partial H}{\partial n_\gamma}\right)_{T,\,p,\,n_\beta} dn_\gamma$$

and represent the first law in the following form:

$$d\Phi = \left(\frac{\partial H}{\partial T}\right)_{p,\,n_\gamma} dT + \left[\left(\frac{\partial H}{\partial p}\right)_{T,\,n_\gamma} - v\right] dp + \sum_\gamma \left(\frac{\partial H}{\partial n_\gamma}\right)_{T,\,p,\,n_\beta} dn_\gamma \tag{9.42}$$

Here the last term on the right-hand side of Eq. (9.42) represents the change in enthalpy of the system attending the change in the amounts of the substances. We now introduce the notation for the partial molar enthalpy of substance γ:

$$\left(\frac{\partial H}{\partial n_\gamma}\right)_{T,\,p,\,n_\beta} \equiv \bar{h}_\gamma \tag{9.43}$$

and divide the quantity dn_γ into two parts: (1) $d_i n_\gamma$ which is the change due to a chemical reaction taking place within the system; (2) $d_e n_\gamma$ which represents the amount of substance supplied to the system from the environment. We shall now divide the total energy flux $d\Phi$ into the heat flux and the mass flux (the transfer of substance to the system), i.e., the convection-diffusion flux:

$$d\Phi_{\text{heat}} = \left(\frac{\partial H}{\partial T}\right)_{p,\,n_\gamma} dT + \left[\left(\frac{\partial H}{\partial p}\right)_{T,\,n_\gamma} - v\right] dp + \sum_\gamma \bar{h}_\gamma d_i n_\gamma \tag{9.44}$$

and

$$d\Phi_{cd} = \sum_\gamma \bar{h}_\gamma d_e n_\gamma \tag{9.45}$$

Relation (9.45) expresses the enthalpy flux supplied by the substance from the surroundings.

9.7. The Production of Entropy in Open Systems. Fluxes

According to the second law, in the interior of any system, either open or closed, the entropy can only be created but it cannot be destroyed, i.e.,

$$d_i S \geqslant 0 \tag{9.46}$$

For an open system as well as a closed system we should speak of the entropy balance:

$$dS = d_e S + d_i S \tag{9.47}$$

where $d_e S$ is the entropy transported to the system during the time dt, and $d_i S$ is the entropy created within the system. But for closed systems $d_e S = \delta Q/T$. In the case of open systems one should take into account the entropy introduced into the system by the substance transferred from the surroundings.

If the system is not uniform with respect to temperature, then it must be split into small volumes with constant temperature and the total entropy must be evaluated by integration:

$$S = \int_v \bar{S}_v \delta v \tag{9.48}$$

where $\bar{S}_v$ is the local entropy per unit volume in each volume element. Of course, speaking more exactly, $\bar{S}_v$ is the entropy of the unit volume of a homogeneous system with temperature and concentrations that are inherent in the volume element of a heterogeneous system. Since the condition (9.48) must be realized within any system, it is also valid for each volume element of a heterogeneous system.

Further in the text we shall deal with the rate of production of entropy in the unit volume of the system, retaining the previous notation, σ_v, which has been previously applied to the entire system, and adding only the subscript v. In the simplest case of a homogeneous system

$$\sigma_v = \frac{1}{v}\frac{d_iS}{dt}$$

If the only irreversible process taking place in the system is a chemical reaction, then, in accordance with Eq. (9.32), we can write:

$$\sigma_{v(\text{chem})} = \mathbf{A}\,\frac{w_v}{T} \geqslant 0 \tag{9.49}$$

where **A** is the affinity of the chemical reaction; w_v is the rate per unit volume, i.e., $w_v = (1/v)\, d\xi/dt$, if ξ is a chemical variable (the extent of reaction); v is the volume of the system. Several (say, r) reactions may, however, proceed simultaneously in the system. Then expression (9.49) should be generalized:

$$\sigma_{v(chem)} = \sum_r \mathbf{A}_r w_{vr}/T \geqslant 0 \tag{9.50}$$

where the sum is extended over all the reactions.

The most remarkable feature of the inequality (9.50) consists in the following. The sum $\mathbf{A}_r w_{vr}$ over all the reactions must be positive. At the same time, the individual terms of the sum, say $\mathbf{A}_1 w_{v1}$, may also be negative provided that the sum of the remaining terms is large enough to provide the condition (9.50). In this way, we deduce the concept of the possible connection between the fluxes. In chemistry, this manifests itself in the phenomenon of coupled (or induced) reactions which proceed with a negative affinity, i.e., at constant T and p and with an increase in the Gibbs free energy.*

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* The thermodynamic coupling of reactions plays an especially important part in living systems. Prigogine and Defay (*Chemical Thermodynamics*, Longmans, London, 1954, p. 42) cite, as an example, the synthesis of urea coupled with the combustion of glucose in the liver. This synthesis may be represented schematically by

$$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O \quad \mathbf{A}_1 = -11.0 \text{ kcal}$$

(coupled reaction)

$$\frac{1}{6} C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \quad \mathbf{A}_2 = +115.0 \text{ kcal}$$

(coupling reaction)

Here the rate of the coupled reaction cannot exceed a certain upper limit, *obtained from* (9.50), *i.e.,*

$$\mathbf{A}_1\omega_1 + \mathbf{A}_2\omega_2 \geqslant 0 \quad \text{and} \quad \omega_1 \leqslant \frac{\mathbf{A}_2}{\mathbf{A}_1}\,\omega_2.$$

Analogously, we can consider the production of entropy associated simultaneously with diffusion and flow of heat (this will be done at a later time). Here relations between various kinds of fluxes may appear. For example, thermal diffusion is an example of the relation between the heat and diffusion fluxes. Nevertheless, σ_{total} is always uniquely greater than zero.

9.8. Gibb's Equation and the Entropy Balance

From what has been said in the preceding section it follows that the entropy balance plays a fundamental role in the methods of nonequilibrium (irreversible) thermodynamics. In a general case, the setting-up of such a balance is based on the Gibbs equation, which may be written for an open system in the form

$$T\,dS = dU + p\,dv - \sum_{\gamma} \mu_\gamma\, dn_\gamma \tag{9.51}$$

where the differentials express the change of the corresponding functions during time *dt*. Or, dividing by the temperature,

$$dS = \frac{dU}{T} + \frac{p}{T}\,dv - \sum_{\gamma} \frac{\mu_\gamma}{T}\, dn_\gamma$$

For an open system we should separate, as has been done in the preceding sections, the total dn_γ into $d_e n_\gamma$ and $d_i n_\gamma$. Here, according to Eq. (9.19), $d_i n_\gamma = \nu_\gamma d\xi$. Recalling also relation (9.21) between the affinity and the algebraic sum of the chemical potentials of the participants in reaction (9.18), we rewrite Eq. (9.51):

$$dS = \frac{dU}{T} + \frac{p}{T}\,dv - \sum_{\gamma} \frac{\mu_\gamma}{T}\, d_e n_\gamma + \frac{A\,d\xi}{T} \tag{9.52}$$

The first two terms on the right-hand side are, however, equal, in accordance with Eq. (9.38), to the entropy balance for an open system divided by the temperature, and therefore

$$dS = \frac{d\Phi}{T} - \sum_{\gamma} \frac{\mu_\gamma}{T}\, d_e n_\gamma + \frac{A\,d\xi}{T} \tag{9.53}$$

This total entropy change consists of the part supplied from the environment, i.e.,

$$d_e S = \frac{d\Phi}{T} - \sum_{\gamma} \frac{\mu_\gamma}{T}\, d_e n_\gamma \tag{9.54}$$

and of the entropy production within the system due to a chemical reaction in this particular case:

$$d_i S = \frac{A\,d\xi}{T} \tag{9.55}$$

Thus, according to Eq. (9.54), the entropy transported to an open system from the surroundings is associated with the energy and mass fluxes that are transferred to the system.

However, the energy flux itself, $d\Phi$, includes the part transported by the substance [see (9.38)], and it is expedient to separate the pure heat flux, dJ_h, from it by subtracting the enthalpy transported by the substance:

$$dJ_h = d\Phi - \sum_\gamma \bar{h}_\gamma d_e n_\gamma \qquad (9.56)$$

where $\bar{h}_\gamma$ iss the partial molar enthalpy of component γ. On the whole the um on the right-hand side of Eq. (9.56) represents precisely the enthalpy flux transported by the substance. Combining Eqs. (9.53) and (9.56), we find that

$$dS = \frac{dJ_h}{T} + \sum_\gamma \frac{\bar{h}_\gamma - \mu_\gamma}{T} d_e n_\gamma + \frac{A\, d\xi}{T} \qquad (9.57)$$

but

$$S = (H - G)/T \quad \text{and} \quad (\partial S/\partial n_\gamma)_{T,\,p,\,n_\beta} = \bar{S}_\gamma = (\bar{h}_\gamma - \mu_\gamma)/T$$

Hence.

$$dS = \frac{dJ_h}{T} + \sum_\gamma \bar{S}_\gamma d_e n_\gamma + \frac{A d\xi}{T} \qquad (9.58)$$

where $\bar{S}_\gamma$ is the partial molar entropy of component γ in the system; the second term on the right-hand side of Eq. (9.58) represents explicitly the entropy transported to the system with the substance.

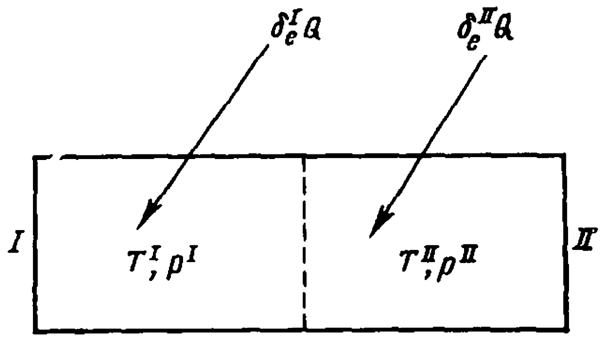

Fig. 9.1. Setting up an entropy balance for a heterogeneous system.

We now turn to the entropy balance in a discontinuous system with different temperatures, pressures, and chemical potentials. Limiting ourselves for the present to a simpler case, we shall consider a system which is closed on the whole but consists of two parts, I and II, with the corresponding values of pressure and temperature: p^{I}, T^{I} and p^{II} and T^{II} (Fig. 9.1). The parts I and II of the system receive the heat fluxes $\delta_e^I Q$ and $\delta_e^{II} Q$ from the surroundings. No substance is transferred to the system—it is closed by condition. However, the parts I and II can exchange matter and are open with respect to each other. For the internal exchange of energy we may write:

$$d_i^{II}\Phi = -d_i^I\Phi \qquad (9.59)$$

At the same time, the substance transferred from one phase to the other will be considered to be supplied to a given phase from the surroundings. Thus,

$$d_e^{II} n_\gamma = -d_e^I n_\gamma \tag{9.60}$$

The entropy balance for a large system will be expressed by the following relation:

$$dS = \frac{\delta_e^I Q}{T^I} + \frac{\delta_e^{II} Q}{T^{II}} + d_i\Phi\left(\frac{1}{T^{II}} - \frac{1}{T^I}\right) + \\ + \sum_\gamma \left(\frac{\mu_\gamma^I}{T^I} - \frac{\mu_\gamma^{II}}{T^{II}}\right) d_e n_\gamma + \frac{A^I\, d\xi^I}{T^I} + \frac{A^{II}\, d\xi^{II}}{T^{II}} \tag{9.61}$$

Here we see clearly the external and internal components of the total entropy change. Namely, the entropy flux transported from the surroundings is given by

$$d_e S = \delta_e^I Q/T^I + \delta_e^{II} Q/T^{II}$$

and the production of entropy is expressed by the sum

$$d_i S = d_i\Phi\left(\frac{1}{T^{II}} - \frac{1}{T^I}\right) + \sum_\gamma \left(\frac{\mu_\gamma^I}{T^I} - \frac{\mu_\gamma^{II}}{T^{II}}\right) d_e n_\gamma + \\ + \frac{A^I\, d\xi^I}{T^I} + \frac{A^{II}\, d\xi^{II}}{T^{II}} \tag{9.62}$$

In Eq. (9.62) the last two terms are associated with a chemical reaction, and the first two terms express the entropy production due to the energy and mass fluxes.

The example considered here may apply to systems with a distinct boundary surface. Here, apart from the well-known difference of the values of $1/T$ [see Eq. (9.35)], there appears the difference in the values of μ_γ/T which changes to the gradient (μ_γ/T) in a continuous system.

II. DISCONTINUOUS SYSTEMS

9.9. Material and Energy Balances

In this section we shall deal with systems which have no distinct boundary surfaces and which cannot yet be regarded as being homogeneous, i.e., systems in which the properties change continuously from point to point. For each point of such a system we can determine, for any extensive property θ (mass, energy, entropy), its *localized** *intensive* value θ_v with the aid of the following relation:

$$\theta_v = \frac{\delta\theta}{\delta v} \tag{9.63}$$

The quantity θ_v will be the density of the property θ and it is related in the following manner to the quantity θ_m calculated per unit mass in a given volume element:

$$\theta_v = \frac{\delta\theta}{\delta v} = \frac{\delta\theta}{\delta m}\,\frac{\delta m}{\delta v} = \theta_m \rho \tag{9.64}$$

where $\rho = \delta m/\delta v$ is the density expressed by the mass per unit volume element.

In the derivation of the basic equation for the rate of production of entropy arising from a chemical reaction, diffusion, heat transfer and other irreversible processes the setting-up of various kinds of balance plays an important role.

In studying diffusion processes, let us first define *the velocity of the centre of mass* ω of a liquid or gaseous mixture, contained in the volume element δv, by the following relation:

$$\omega\rho = \sum_{\gamma} \rho_\gamma \omega_\gamma \tag{9.65}$$

where ρ_γ is the mass of component γ of the mixture in the unit volume; ω_γ is the velocity of motion of that component. If the velocities of various components are equal to the velocity of the centre of mass, one speaks of the absence of diffusion.

When the velocities ω_γ differ from ω, *the rate of diffusion of the component*, Δ_γ, is determined:

$$\Delta_\gamma = \omega_\gamma - \omega \tag{9.66}$$

Since $\rho = \sum_{\gamma} \rho_\gamma$, from Eqs. (9.65) and (9.66) we obtain the relation between the rates of diffusion of the individual components:

$$\sum_{\gamma} \rho_\gamma \Delta_\gamma = 0 \tag{9.67}$$

If we consider the change in the property θ in a moving flux in unit volume in the direction of motion of its centre of mass, then this change can be represented as the sum of the local change in the fixed volume element and the change associated with the flow along the line of motion (Fig. 9.2) where there takes place a spatial change in θ:

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* The systems under consideration are on the whole non-equilibrium systems. From the standpoint of statistics, for example, they do not obey the Maxwell-Boltzmann distribution law and, hence, in general their thermodynamic properties cannot be determined. We can, however, imagine a system separated into volume elements, so that the distribution law is observed within each volume element and the thermodynamic properties have certain localized values within each volume element.

$$\frac{d\theta}{dt} = \frac{\partial\theta}{dt} + \frac{\partial\theta}{dl}\frac{\partial l}{dt} \tag{9.68}$$

On the basis of this relation we define the operator d/dt as the variation of the property with time in the direction of motion of the centre of mass—it is this operator that will be related to the operator of the local change with time in the following manner:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \omega \text{ grad} \tag{9.69}$$

Here the velocity ω is substituted for $\partial l/\partial t$, and $\partial\theta/\partial l$ is replaced by the gradient of the scalar field of a certain property.

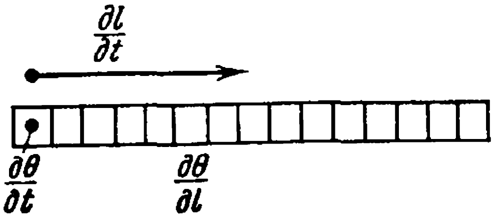
$\frac{\partial l}{\partial t}$
$\frac{\partial\theta}{\partial t}$
$\frac{\partial\theta}{\partial l}$

Fig. 9.2. The change in the property θ in a volume element in a flow.

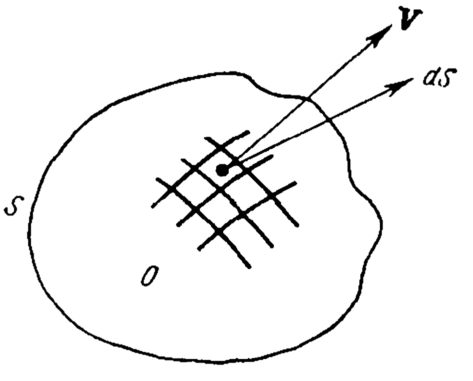

Fig. 9.3. Defining the concepts of the vector flux and divergence.

Before writing down the relation for the local change of θ with time, we remind the reader of the concepts of fluxes and of the vector divergence field. We draw in a vector field **V** (it is useful to visualize the velocity field of a flowing liquid) some closed surface S and determine the flux of the vector **V** through this surface. Since in the various portions of this surface the vector **V** may have different magnitudes and different directions, it is necessary to divide the entire surface into elementary areas dS (Fig. 9.3) of such a small size that within any of these areas the vector **V** has the same magnitude and direction.

By the definition of the vector flux, the elementary flow through each area dS is equal to $dN = dS\mathbf{V} \cos (dS\mathbf{V})$ or, in the vector representation, $dN = (\mathbf{V}\, dS) = \mathbf{V}_n\, dS$, where $\mathbf{V}_n$ is the normal component of the vector **V** with respect to the area. If we assume that the positive normal is directed outward away from the surface, then the positive dN will signify the outflow of the liquid from the volume O enclosed within the surface S, and the negative dN the inflow of the liquid into this volume. The total flow through the entire surface $N = \oint\limits_S (\mathbf{V}_n\, dS)$. Here the integral with a circle means the integration over the entire closed surface.

Let us now divide this flux by the volume O bounded by the surface S:

$$\frac{N}{O} = \oint (\mathbf{V}_n\, dS) \Big/ \int dO$$

as a result of which we obtain a certain mean value of the flux N per unit volume enclosed within the surface S. If we reduce the volume under consideration indefinitely, then in the limit for an infinitesimal volume in the neighbourhood of the point p of the field we shall obtain a certain value, which is called the divergence of the vector $\mathbf{V}$ at that point:

$$\lim_{O\to 0}\left[\frac{\oint \mathbf{V}_n\, dS}{O}\right] \equiv \operatorname{div}\mathbf{V}$$

The quantity div $\mathbf{V}$ is a scalar quantity and forms a scalar field in the given vector field. In the Cartesian coordinates

$$\operatorname{div}\mathbf{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z}$$

Next, according to Prigogine (1947), we can write the variation of each of the quantities θ_v with time, which is defined by relation (9.63) in the form of a local balance:

$$\frac{\partial \theta_v}{\partial t} = -\operatorname{div}\Phi[\theta] + \sigma[\theta] \tag{9.70}$$

where div Φ $[\theta]$ is the flux of θ emerging from the unit volume element; $\sigma[\theta]$ is the so-called density of the θ sources in the same volume if the property θ arises in some way within the volume considered. In other words, $\sigma[\theta]$ will express the amount of θ produced per second per unit volume in the given volume element.

Applying relation (9.70) to the local balance for the total mass, we find that

$$\frac{\partial \rho}{\partial t} = -\operatorname{div}\rho\omega \tag{9.71}$$

Here account is taken of the law of conservation of the total mass, i.e., the absence of its sources. Equation (9.71) is equivalent to the continuity equation in hydrodynamics.

On the other hand, the mass of an individual component γ may vary because of a chemical reaction that may take place in the system. Therefore, the local balance of ρ_γ has the form

$$\frac{\partial \rho_\gamma}{\partial t} = -\operatorname{div}\rho_\gamma\omega_\gamma + \nu_\gamma M_\gamma w_v$$

where the second term represents the mass of component γ formed in unit volume per unit time. Taking into account the definition of the rate of diffusion $\Delta_\gamma = \omega_\gamma - \omega$ (9.66) and also the rules of calculation of the divergence, we obtain the following expression from the preceding one:

$$\frac{\partial \rho_\gamma}{\partial t} = -\operatorname{div} \rho_\gamma \omega - \operatorname{div} \rho_\gamma \Delta_\gamma + \nu_\gamma M_\gamma \omega_v \tag{9.72}$$

where w_v is the rate of reaction per unit volume; ν_γ is the stoichiometric coefficient of component γ in this reaction; M_γ is the molar mass of component γ. In relation (9.72) it is assumed, for simplicity, that component γ participates only in one reaction. But if several (r) reactions take place, the last term in (9.72) is written as the sum over all the r reactions: $\sum_r \nu_{\gamma r} M_\gamma w_{vr}$.

Further, we write the balance for the mass fraction of component γ:

$$N_\gamma = \frac{\rho_\gamma}{\rho} \tag{9.73}$$

or $\rho_\gamma = N_\gamma \rho$. Differentiating the last relation with respect to time, we obtain:

$$\frac{\partial \rho_\gamma}{\partial t} = N_\gamma \frac{\partial \rho}{\partial t} + \rho \frac{\partial N_\gamma}{\partial t} \tag{9.74}$$

but, according to Eq. (9.71), $\partial\rho/\partial t = -\operatorname{div} \rho\omega$, and instead of the local derivative $\partial N_\gamma/\partial t$ we can write, in accordance with Eq. (9.69), the relation including dN_γ/dt, which is the total change of N_γ with time, i.e., $\partial N_\gamma/\partial t = dN_\gamma/dt - \omega \operatorname{grad} N_\gamma$. We now write instead of Eqs. (9.72) and (9.74):

$$\begin{aligned}\frac{\partial \rho_\gamma}{\partial t} &= -N_\gamma \operatorname{div} \rho\omega + \rho\left[\frac{dN_\gamma}{dt} - \omega \operatorname{grad} N_\gamma\right] = \\ &= -\operatorname{div} \rho_\gamma \omega - \operatorname{div} \rho_\gamma \Delta_\gamma + \nu_\gamma M_\gamma w_v\end{aligned} \tag{9.75}$$

From vector algebra we know the expression for the divergence of the product of the scalar quantity U by the vector $\mathbf{V}$:

$$\operatorname{div}(U\mathbf{V}) = U \operatorname{div} \mathbf{V} + \mathbf{V} \operatorname{grad} U$$

Applying this expression to $\operatorname{div} \rho\omega$ and $\operatorname{div} \rho_\gamma\omega$, we obtain:

$$\begin{aligned}-N_\gamma \rho \operatorname{div} \omega - N_\gamma \omega \operatorname{grad} \rho + \rho \frac{dN_\gamma}{dt} - \rho\omega \operatorname{grad} N_\gamma = \\ = -\rho_\gamma \operatorname{div} \omega - \omega \operatorname{grad} \rho_\gamma - \operatorname{div} \rho_\gamma \Delta_\gamma + \nu_\gamma M_\gamma w_v\end{aligned}$$

Here the first terms of the expressions on the right- and left-hand sides are equal and cancel, and the term on the right-hand side,

$-\omega$ grad $\rho_\gamma = -\omega$ grad $N_\gamma\rho$, can, by means of the rules of calculation (vector algebra) of the gradients of the scalars N_γ and ρ, be transformed to $-\omega N_\gamma$ grad $\rho - \omega\rho$ grad N_γ. But there are precisely such terms on the left-hand side too. Cancelling the like terms, we obtain the balance equation for the mass fraction of the component:

$$\rho \frac{dN_\gamma}{dt} = \operatorname{div} \rho_\gamma \Delta_\gamma + \nu_\gamma M_\gamma w_v \tag{9.76}$$

Here the derivative $\partial N_\gamma/\partial t$ represents the variation of the mass fraction of component γ with time which is caused either by a chemical reaction proceeding at a velocity w_v or by a diffusion flux, i.e., by the difference of the velocities of motion of the component and the centre of mass [see relation (9.66)].

In an analogous manner we can relate the local variation of any thermodynamics property θ_v with time per unit volume to the change, in the direction of motion of the centre of mass, of the amount of $\theta_m = \theta_v/\rho$ per unit mass. Here use is made of the operator $d/dt = \partial/\partial t + \omega$ grad (9.69) and the value of the derivative $\partial\rho/\partial t = -\operatorname{div} \rho\omega$ (9.71). Thus, the application of the operator (9.69) to θ_v allows one to write down its total change with time:

$$\frac{d\theta_v}{dt} = \frac{\partial\theta_v}{\partial t} + \omega \operatorname{grad} \theta_v$$

or, since $\theta_v = \theta_m\rho$,

$$\rho \frac{d\theta_m}{dt} + \theta_m \frac{d\rho}{dt} = \frac{\partial\theta_v}{\partial t} + \omega \operatorname{grad} \theta_v$$

The derivative $d\rho/dt$ implies the dependence of the density ρ on time during motion; we replace it by the local variation of ρ once again with the aid of relation (9.69):

$$\rho \frac{d\theta_m}{dt} = \frac{\partial\theta_v}{\partial t} - \theta_m \left(\frac{\partial\rho}{\partial t} + \omega \operatorname{grad} \rho \right) + \omega \operatorname{grad} \theta_v$$

The local derivative of the total density $\partial\rho/\partial t$ can now be replaced by the divergence $-\operatorname{div} \rho\omega$ [relation (9.71)]:

$$\rho \frac{d\theta_m}{dt} = \frac{\partial\theta_v}{\partial t} + \theta_m \operatorname{div} \rho\omega - \theta_m\omega \operatorname{grad} \rho + \omega \operatorname{grad} \theta_v \tag{9.77}$$

Since $\rho = \theta_v/\theta_m$, the second term on the right-hand side transforms to

$$\theta_m \operatorname{div} \frac{\theta_v}{\theta_m} \omega = \frac{\theta_m}{\theta_m} \operatorname{div} \theta_v\omega + \theta_m\theta_v\omega \operatorname{grad} \frac{1}{\theta_m}$$

Thus, relation (9.77) can be rewritten as

$$\rho \frac{d\theta_m}{dt} = \frac{\partial \theta_v}{\partial t} + \operatorname{div} \theta_v \omega + \\ + \left\{ \theta_m \theta_v \omega \operatorname{grad} \frac{1}{\theta_m} - \theta_m \omega \operatorname{grad} \rho + \omega \operatorname{grad} \theta_r \right\} \tag{9.78}$$

While considering the last three terms enclosed in braces in expression (9.78) we see that their sum is equal to zero. Indeed, the first of these terms

$$\theta_m \theta_v \omega \operatorname{grad} \frac{1}{\theta_m} = -\frac{\theta_m \theta_v}{\theta_m^2} \omega \operatorname{grad} \theta_m = -\rho\omega \operatorname{grad} \theta_m$$

and the last one, i.e., the third term, can be transformed to in the following manner:

$$\omega \operatorname{grad} \theta_v = \omega \operatorname{grad} \theta_m \rho = \omega \theta_m \operatorname{grad} \rho + \omega \rho \operatorname{grad} \theta_m$$

Thus, instead of the expression in braces, we obtain:

$$-\rho\omega \operatorname{grad} \theta_m - \theta_m \omega \operatorname{grad} \rho + \omega \theta_m \operatorname{grad} \rho + \omega \rho \operatorname{grad} \theta_m = 0$$

Hence, for the balance of the amount of θ_m we shall finally have:

$$\rho \frac{d\theta_m}{dt} = \frac{\partial \theta_v}{\partial t} + \operatorname{div} \theta_v \omega \tag{9.79}$$

Turning now to the energy balance, we write, first, the equation for the flow of a non-viscous liquid, using the local velocity of the centre of mass in the following form:

$$\rho \frac{d\omega}{dt} = \sum_{\gamma} \rho_\gamma F_\gamma - \operatorname{grad} p \tag{9.80}$$

where F_γ is the external force acting on the unit mass of component γ and, hence, $\sum \rho_\gamma F_\gamma$ is the total external force acting on the unit volume of the liquid; it is summed up with the internal force equal to the negative pressure gradient. From the equation of motion (9.80) we obtain the balance of the kinetic energy per unit mass:

$$l_m = \omega^2/2 \Big/ \frac{dl_m}{dt} = \omega \frac{d\omega}{dt} = \omega \frac{\sum \rho_\gamma F_\gamma}{\rho} - \frac{\omega \operatorname{grad} p}{\rho}$$

or, introducing the notation which includes the total external force F, i.e., $F\rho = \sum \rho_\gamma F_\gamma$ [compare also with Eq. (9.65)],

$$\frac{dl_m}{dt} = F\omega - \frac{\omega \operatorname{grad} p}{\rho} \tag{9.81}$$

We also include the potential energy in the balance. If the volume element of the substance, δv, is flowing in an external field, the balance of its potential will be expressed thus:

$$\frac{dO_m}{dt} = -F\omega \tag{9.82}$$

where O_m is the potential energy of the unit mass; $F\omega$ is the work done by the force F in unit time.

In the absence of diffusion one may consider the mass element as a closed system and write for it the balance of the internal energy in the following simple form of the first law:

$$\frac{dU_m}{dt} = -\frac{1}{\rho} \operatorname{div} W - p\frac{dv_m}{dt} \tag{9.83}$$

where U_m is the internal energy of the unit mass: $1/\rho = v_m$ is the volume of the unit mass; W is the heat flux across the unit surface that bounds the system under consideration. The heat flux is related to the amount of heat $\delta Q/\partial t$ received by the mass element along the line of its flow:

$$\frac{\delta Q}{\partial t} = -\frac{1}{\rho} \operatorname{div} W \tag{9.84}$$

Thus, the first term on the right-hand side of relation (9.83) represents the amount of heat transferred to the mass element per unit time, while the second term represents the mechanical work done upon it (i.e., the mass element). Let us now write the balance of the total energy $\varepsilon_m = l_m + U_m + O_m$ per unit mass:

$$\frac{d\varepsilon_m}{dt} = F\omega - \frac{\omega \operatorname{grad} p}{\rho} - F\omega - \frac{1}{\rho} \operatorname{div} W - p\frac{d\,(1/\rho)}{dt} \tag{9.85}$$

from which, using the transformation (9.79), we pass over to the local energy balance per unit volume $\partial\varepsilon_v/\partial t$:

$$\frac{\partial\varepsilon_m}{\partial t} = \frac{1}{\rho}\frac{\partial\varepsilon_v}{\partial t} + \frac{1}{\rho} \operatorname{div} \omega\varepsilon_v = -\frac{1}{\rho} \operatorname{div} W - p\frac{d\,(1/\rho)}{dt} - \omega\frac{\operatorname{grad} p}{\rho}$$

or, solving for $\partial\varepsilon_v/\partial t$,

$$\frac{\partial\varepsilon_v}{\partial t} = -\operatorname{div} W - \operatorname{div} \omega\varepsilon_v - \rho p\frac{d\,(1/\rho)}{dt} - \omega \operatorname{grad} p \tag{9.86}$$

Rearranging the last expression, we note, first, that the third term on the right-hand side is equal to $(p/\rho)\, d\rho/dt$, i.e., contains the density balance in flow. Since we are speaking of the local energy balance, this term is transformed, using the operator (9.69) and taking account of Eq. (9.71):

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \omega \operatorname{grad} \rho = -\operatorname{div} \rho\omega + \omega \operatorname{grad} \rho =$$

$$= -\rho \operatorname{div} \omega - \omega \operatorname{grad} \rho + \omega \operatorname{grad} \rho = -\rho \operatorname{div} \omega$$

The last two terms on the right-hand side of Eq. (9.86) are written in the form:

$$-\rho p\frac{d\,(1/\rho)}{dt} - \omega \operatorname{grad} p = -p \operatorname{div} \omega - \omega \operatorname{grad} p = -\operatorname{div} p\omega$$

Hence, we arrive at the local balance of the total energy:

$$\frac{d\varepsilon_v}{\partial t} = -\operatorname{div}(\omega\varepsilon_v + W + p\omega) \tag{9.87}$$

from which it follows that in the volume element under consideration there are no sources of the total energy. The total energy remains constant.

If diffusion occurs in the system, the expression for the internal-energy balance (9.83) has the form:

$$\frac{dU_m}{dt} = -\frac{1}{\rho}\operatorname{div} W - p\,\frac{dv_m}{dt} + \frac{1}{\rho}\sum_{\gamma}\rho_\gamma\Delta_\gamma F_\gamma \tag{9.88}$$

where F_γ is the force acting on the unit mass of component γ, and $\Delta_\gamma = \omega_\gamma - \omega$, in accordance with Eq. (9.66), is its rate of diffusion. On the whole, the last term may be regarded as the work done by the external forces per unit time to effect the diffusion separation of the components of the mixture in its unit mass. It should be remarked that the total-energy balance will be the same as in the case of a system undergoing no diffusion.

9.10. The Local Entropy Balance for Continuous Systems. The Onsager Equations

We shall now turn to the thermodynamics of irreversible processes proper in continuous systems. We use, as the basis, the Gibbs fundamental equation for the entropy change in an open homogeneous system:

$$T\,dS = dU + p\,dv - \sum_{\gamma}\mu_\gamma\,dm_\gamma \tag{9.89}$$

in the notation which differs from the ordinary one only in the definition of the chemical potential not per mole but per unit mass. We divide this equation by the total mass of the system, thereby reducing it to unit mass:

$$T\,dS_m = dU_m + p\,dv_m - \sum_{\gamma}\mu_\gamma\,dN_\gamma \tag{9.90}$$

where the chemical potential is evaluated locally by the following relation:

$$\mu_\gamma = -T\left(\frac{\partial S_m}{\partial N_\gamma}\right)_{U_m, v_m, N_\beta} \tag{9.91}$$

According to the basic assumption of the thermodynamics of irreversible processes Eq. (9.90) remains valid in a certain region beyond the equilibrium and it may be written in the following form for the changes in the mass element flowing in the direction of motion of the centre of mass:

$$T\frac{dS_m}{dt}=\frac{dU_m}{dt}+p\frac{dv_m}{dt}-\sum_{\gamma}\mu_\gamma\frac{dN_\gamma}{dt} \tag{9.92}$$

This assumption can be confirmed by the methods of statistical mechanics for a relatively wide range of irreversible situations. As a matter of fact, as has already been said, this means that in a state, which is on the whole non-equilibrium, there are realized local equilibria in accordance with the Maxwell-Boltzmann distribution law.

Further, we rearrange Eq. (9.92), using the mass balance (9.76), the internal-energy balance (9.88) and relation (9.79). First, utilizing Eq. (9.79) and the balance of U_m, i.e., relation (9.88), we write:

$$\begin{aligned}T\frac{dS_m}{dt}&=\frac{T}{\rho}\frac{\partial S_v}{\partial t}+\frac{T}{\rho}\operatorname{div}S_v\omega=-\frac{1}{\rho}\operatorname{div}W-p\frac{dv_m}{dt}+\\&+\frac{1}{\rho}\sum_{\gamma}\rho_\gamma\Delta_\gamma F_\gamma+p\frac{dv_m}{dt}-\sum_{\gamma}\mu_\gamma\frac{dN_\gamma}{dt}\end{aligned} \tag{9.93}$$

or, solving for $\partial S_v/\partial t$:

$$\frac{\partial S_v}{\partial t}=-\operatorname{div}S_v\omega-\frac{1}{T}\operatorname{div}W+\frac{1}{T}\sum_{\gamma}\rho_\gamma\Delta_\gamma F_\gamma-\frac{\rho}{T}\sum_{\gamma}\mu_\gamma\frac{dN_\gamma}{dt} \tag{9.94}$$

We now transform the last term on the right-hand side on the basis of Eq. (9.76):

$$\begin{aligned}-\frac{\rho}{T}\sum_{\gamma}\mu_\gamma\frac{dN_\gamma}{dt}&=-\frac{1}{T}\sum_{\gamma}\mu_\gamma\Big(-\operatorname{div}\rho_\gamma\Delta_\gamma+\sum_{r}\nu_{\gamma r}M_\gamma w_{vr}\Big)=\\&=\sum_{\gamma}\frac{\mu_\gamma}{T}\operatorname{div}\rho_\gamma\Delta_\gamma-\frac{1}{T}\sum_{\gamma}\mu_\gamma\sum_{r}\nu_{\gamma r}w_{vr}M_\gamma\end{aligned} \tag{9.95}$$

We now rewrite the first term on the right-hand side of Eq. (9.95) in conformity with the rules of evaluation of the divergence:

$$\begin{aligned}-\frac{\rho}{T}\sum_{\gamma}\mu_\gamma\frac{dN_\gamma}{dt}&=\sum_{\gamma}\operatorname{div}\frac{\mu_\gamma}{T}\rho_\gamma\Delta_\gamma-\\&-\sum_{\gamma}\rho_\gamma\Delta_\gamma\operatorname{grad}\frac{\mu_\gamma}{T}-\frac{1}{T}\sum_{\gamma}\mu_\gamma\sum_{r}\nu_{\gamma r}M_\gamma w_{vr}\end{aligned}$$

Focusing our attention on the fact that in Eq. (9.94) $(1/T)\operatorname{div}W=$ $=\operatorname{div}(W/T)-W\operatorname{grad}(1/T)$, we rewrite the local entropy balance thus:

$$\frac{\partial S_v}{dt} = -\operatorname{div}\left(S_v\omega + \frac{W}{T} - \sum_\gamma \rho_\gamma \Delta_\gamma \frac{\mu_\gamma}{T}\right) + W \operatorname{grad}\frac{1}{T} +$$

$$+ \frac{1}{T}\sum_\gamma \rho_\gamma \Delta_\gamma F_\gamma - \sum_\gamma \rho_\gamma \Delta_\gamma \operatorname{grad}\frac{\mu_\gamma}{T} - \frac{1}{T}\sum_\gamma \mu_\gamma \sum_r \nu_{\gamma r} M_\gamma w_{vr} \tag{9.96}$$

or

$$\frac{\partial S_v}{\partial t} = -\operatorname{div}\left(S_v\omega + \frac{W}{T} - \sum_\gamma \rho_\gamma \Delta_\gamma \frac{\mu_\gamma}{T}\right) +$$

$$+ \frac{1}{T}\sum_\gamma \rho_\gamma \Delta_\gamma \left(F_\gamma - T \operatorname{grad}\frac{\mu_\gamma}{T}\right) + W \operatorname{grad}\frac{1}{T} + \sum_r \frac{A_r w_{vr}}{T} \tag{9.97}$$

This is exactly the sought-for equation for the local entropy balance per unit volume element of an open continuous system, in which heat transfer and diffusion and also r chemical reactions take place. The last term in this equation represents the transformation of the expression $-(1/T)\sum_\gamma \mu_\gamma \sum_r \nu_{\gamma r} M_\gamma w_{vr}$ to Eq. (9.96) summed over all the reactions in which a given component participates. Let us consider the expression for one reaction, namely $-(1/T)\sum_\gamma \mu_\gamma M_\gamma \nu_\gamma w_v = Aw_v/T$, since, according to Eq. (9.89), the chemical potential is defined per unit mass and the product $\mu_\gamma M_\gamma$ will be its value per mole. Therefore, $-\sum_\gamma \mu_\gamma M_\gamma \nu_\gamma = A$, i.e., is equal to the chemical affinity of a given reaction.

Thus, the last term in Eqs. (9.96) and (9.97) corresponds to the rate of production of entropy in unit volume due to r chemical reactions, which proceed at rates w_r. Let us compare Eq. (9.97) with the initial equation (9.70) derived by Prigogine for the local balance of an extensive thermodynamic property θ. Whereas Eqs. (9.71) and (9.87) for the total-mass and total-energy balances [these equations are also derived from Eq. (9.70)], did not contain sources of mass and energy in accordance with the laws of conservation, the last three terms on the right-hand side of Eq. (9.97) constitute the sum of entropy sources. On the other hand, in accordance with what has been said above, in Eq. (9.97) the relation

$$J_S = S_v\omega + \frac{W}{T} - \sum_\gamma \rho_\gamma \Delta_\gamma \frac{\mu_\gamma}{T} \tag{9.98}$$

represents the entropy flux transported to the volume element from the surroundings. Thus, this equation shows that the volume element can receive entropy from the surroundings as a result of the material entering at velocity ω due to the heat flux W from the surroundings and also of the diffusion of each of the components at velocity Δ_γ. Using the separation of the total entropy change introduced in Eq. (9.6) into the external and internal parts, we can write:

$$\frac{\partial S_v}{\partial t} = \frac{\partial_e S_v}{\partial t} + \frac{\partial_i S_v}{\partial t}$$

It should be noted that, in accordance with Eqs. (9.97) and (9.98),

$$\frac{\partial_e S_v}{\partial t} = -\operatorname{div} J_S$$

This external cause of the entropy change of the system is of no interest to us and we shall not consider the first term in Eq. (9.97) in the subsequent discussion. Second, the entropy is created within the volume under consideration. This entropy source, which is the key point in irreversible thermodynamics, is also contained in Eq. (9.97) and it may be represented in the form

$$\frac{\partial_i S_v}{\partial t} = \sigma_S = \frac{1}{T}\sum_r \mathrm{A}_r w_{vr} + W \operatorname{grad}\frac{1}{T} + \frac{1}{T}\sum_\gamma \rho_\gamma \Delta_\gamma \left(F_\gamma - T \operatorname{grad}\frac{\mu_\gamma}{T}\right) \geqslant 0 \tag{9.99}$$

This relation expresses the rate of production of entropy per unit time in unit volume of an element in an open continuous system. Equation (9.99) should be rewritten in the following form:

$$T\sigma_S = \sum_r \mathrm{A}_r w_{vr} - \frac{\operatorname{grad} T}{T} W + \sum_\gamma \rho_\gamma \Delta_\gamma \left(F_\gamma - T \operatorname{grad}\frac{\mu_\gamma}{T}\right) \geqslant 0 \tag{9.100}$$

where the cofactors $-\operatorname{grad} T/T$, A_r and $[F_\gamma - T \operatorname{grad} (\mu_\gamma/T)]$ may be regarded as generalized forces that cause the heat flux W, the reaction flux at velocity w_{vr} and the diffusion flux $\rho_\gamma\Delta_\gamma$. The entropy production is thus a bilinear function of the forces and the fluxes caused by them. The term $(1/T) \sum_r \mathrm{A}_r w_{vr}$ expresses the rate of entropy production due to chemical reactions; the relation $(W/T) \times (-\operatorname{grad} T)/T$ is equal to the entropy production per unit time due to the heat or energy flux; and $(1/T) \sum_\gamma \rho_\gamma \Delta_\gamma [F_\gamma - T \operatorname{grad} (\mu_\gamma/T)]$ represents the entropy created by the diffusion flux.

According to the second law of thermodynamics the rate of entropy production is always positive, i.e.,

$$\sigma_S \geqslant 0 \tag{9.101}$$

The second law does not, however, require that each of the terms in σ_S be positive. The coupling of nonequilibrium or irreversible processes can, as has already been mentioned, lead to the appearance of the negative terms of the sum, i.e., to phenomena that create situations of opposite direction as compared with those which are characteristic of the given isolated phenomenon. Thus, generally speaking, the concentration gradient must become equalized, but when irreversible processes are coupled, concentration gradients can be produced.

Let us designate the affinities or generalized forces by X_i and the fluxes by J_i. Equation (9.100) will then assume the form

$$T\sigma_S = \sum_i J_i X_i \geqslant 0 \tag{9.102}$$

The possibilities of thermodynamics itself are in fact exhausted by this equation. The further use of Eq. (9.102) is associated with the assumptions (which go beyond the scope of thermodynamics) concerning the character of the dependence of the fluxes on the forces that generate them. The situation here resembles, to a certain extent, the situation observed in classical thermodynamics, where quite accurate equations that follow from the general laws can practically be utilized only in conjunction with any equation of state, say $pV = nRT$.

The sought-for dependences $J_i = f(X_i)$ are unknown in a general form and therefore one takes into account that at equilibrium no fluxes are present and the forces are equal to zero and expands the function into a Maclaurin's series, writing, for example, for the flux J_i:

$$J_i = f(X_i) = f(0) + X_i f'(0) + X_i^2 \frac{f''(0)}{2!} + X_i^3 \frac{f'''(0)}{3!} + \dots$$

Here, according to what has been said, $f(0) = 0$. If we agree to study systems which are in states not too far away from the state of equilibrium (X_i is small), then we can retain only the linear term of the expansion. Furthermore, one should consider the possible couplings between various fluxes and postulate the following linear relation between the flux J_i and the forces operative in the system:

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \tag{9.103}$$

Here the summation which expresses the dependence of a given flux on the forces operating in the system, is taken over all the irreversible processes. Relation (9.103) is usually called the *Onsager relation* (1931). According to what has been said above, this equation is valid for the so-called linear domain of irreversible thermodynamics, i.e., for systems whose states differ little from the state of equilibrium.

From Onsager's fundamental theorem it follows that within the range of validity of the linear approximation the proportionality factors, the Onsager phenomenological coefficients L_{ik}, must satisfy the condition of symmetry*:

$$L_{ik} = L_{ki} \tag{9.104}$$

Relations (9.104) are called the *Onsager reciprocal relations*. There exist proofs for the Onsager rule which are based on the principle of microscopic reversibility and on the interpretation of the appearance and disappearance of fluctuations by the methods of statistical mechanics (I. Prigogine, 1967). However, we cannot know *a priori* whether all the off-diagonal coefficients L_{ik} really exist. The presence of effective couplings between two irreversible processes can be established only by experiment. But if it has been experimentally found that there is a connection between a given force X_k and a flux J_i, then, according to the Onsager reciprocal relation, there will also exist the reverse coupling, the one between the force X_i and the flux J_k.

On the other hand, there exists a criterion which allows one to reduce *a priori* the number of effective couplings—this is Curie's principle of symmetry. It states that a macroscopic phenomenon in the system never has more elements of symmetry than the cause that produces it. For example, the chemical affinity (which is a scalar quantity) cannot cause a vectorial heat flux and the corresponding coupling coefficient disappears. What has just been said corresponds to the following theorem: a coupling is possible only between phenomena having the same tensor symmetry. However, according to Glansdorf and Prigogine (1970), the requirement of symmetry with respect to couplings of irreversible processes becomes invalid in the so-called nonlinear region, i.e., beyond the range of applicability of Eq. (9.103), when processes and couplings that violate the symmetry become possible. In our discussion we shall confine ourselves to the linear region.

According to the experimental observations of Fourier, Fick, Ohm and others, a flux (or flow) caused by the action of a force is proportional to that force; the diagonal coefficient that appears here is denoted as L_{ii}. All such diagonal coefficients show up on the diagonal of the force matrix in the series of equations (9.103). This equation, however, also implies the statement that the flux J_i may also be caused by the force X_k if the off-diagonal coefficient $L_{ik(i \neq k)}$ is different from zero.

On the whole, the linear law is valid for sufficiently slowly occurring processes when the system is not too far away from the equilibrium state. However, the range of processes covered by phenomenological equations is nevertheless very wide; it includes many processes studied by physics, chemistry, biology, and physiology.

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* Here we are dealing with the Onsager phenomenological coefficients which are characteristic of the most frequently encountered α-type forces. The β-type forces, which are encountered seldom, are represented by the Casimir coefficients. For these forces relation (9.104) changes to the antisymmetric relation: $L_{ik} = -L_{ki}$.

To illustrate the applications of Eqs. (9.102) and (9.103), let us consider two simultaneous irreversible processes, the phenomenological equation for which can be written thus:

$$J_1 = L_{11}X_1 + L_{12}X_2 \text{ and } J_2 = L_{21}X_1 + L_{22}X_2 \qquad (9.105)$$

If the processes under consideration are heat conduction and diffusion, the off-diagonal coefficient L_{ik} is associated with thermal diffusion, i.e., the appearance of a concentration gradient in an originally homogeneous medium under the influence of a temperature gradient.

Expression (9.102) for the rate of entropy production corresponding to the two processes has the following form:

$$T\sigma_S = L_{11}X_1^2 + (L_{12} + L_{21})\, X_1X_2 + L_{22}X_2^2 \geqslant 0 \qquad (9.106)$$

Inequality (9.106) can be satisfied in a general case with the following values of the phenomenological coefficients:

$$L_{11} > 0,\ L_{22} > 0 \qquad (9.107)$$

and

$$(L_{12} + L_{21})^2 < 4L_{11}L_{22} \qquad (9.108)$$

Thus, the diagonal coefficients L_{11} and L_{22} are positive, whereas the off-diagonal coefficients L_{12} and L_{21} may be either positive or negative, their absolute value being limited by relation (9.108). All this is consistent with experimental data, according to which coefficients such as coefficients of thermal conductivity and electric conductivity are always positive, while the thermal-diffusion coefficient, for example, has no definite sign.

9.11. Transport Phenomena and the Rate of Chemical Reactions

For the linear region, two expressions for the rate of entropy production are singled out of Eq. (9.99), since they are independent by virtue of the different symmetries of the phenomena depicted:

(a) one associated with transport phenomena

$$\sigma_t = W\left(-\frac{\operatorname{grad} T}{T^2}\right) + \frac{1}{T}\sum_{\gamma} \rho_\gamma \Delta_\gamma \left(F_\gamma - T \operatorname{grad} \frac{\mu_\gamma}{T}\right) \geqslant 0 \qquad (9.109)$$

(b) the other associated with chemical reactions

$$\sigma_{ch} = \frac{1}{T}\sum_{r} \mathrm{A}_r w_{vr} \geqslant 0 \qquad (9.110)$$

Chemical reactions will be discussed in more detail at a later time. At this point, in connection with relation (9.109) we shall dwell on the question of choice of expressions for forces and fluxes. The point is that, depending on the nature of the problem to be solved, this choice can be made in different ways. Thus, according to Prigogine (1967), instead of the forces X_i and fluxes J_i which enter into expressions (9.102), we may introduce a new series of definitions of forces (the affinity quantities) X_i' which are a linear combination of the previous quantities. Accordingly, it will be necessary to choose a new series of fluxes (velocities) J_i' so that the rate of entropy production remains unchanged, i.e., $T\sigma_s = \sum_i J_i X_i = \sum_i J_i' X_i'$. Let us consider a transformation of this kind with respect to expression (9.109) for the rate of entropy production, associated with transport phenomena. It should also be stressed that the force factor $[F_\gamma - T \operatorname{grad} (\mu_\gamma/T)]$, which corresponds to the diffusion flux $\rho_\gamma\Delta_\gamma$, has been chosen not very correctly since it contains an arbitrary additive constant and therefore has no definite value. Indeed, the term grad (μ_γ/T) contained in the diffusion affinity may be represented as follows:

$$\operatorname{grad}\frac{\mu_\gamma}{T} = \frac{1}{T}\operatorname{grad}\mu_\gamma - \frac{\mu_\gamma}{T^2}\operatorname{grad} T \tag{9.111}$$

Hence, the arbitrary constant contained in the expression for the chemical potential, $\mu_\gamma = RT \ln f_\gamma + C$, appears in the given expression for the diffusion affinity. This can, however, be avoided, first, if we give a new definition of the heat flux by introducing the partial enthalpy of component, h_γ, and the quantity $\sum_\gamma \rho_\gamma\Delta_\gamma h_\gamma$, which is equal to the enthalpy transported by the diffusion flux of the substance. In such a case, we can write the following sum: $W = J_h + \sum_\gamma \rho_\gamma\Delta_\gamma h_\gamma$, where J_h is the so-called reduced heat flux. Then, instead of Eq. (9.109), we may write the following:

$$T\sigma_t = J_h\left(-\frac{\operatorname{grad} T}{T}\right) + \sum_\gamma \rho_\gamma\Delta_\gamma\left(F_\gamma - \frac{h_\gamma}{T}\operatorname{grad} T - T\operatorname{grad}\frac{\mu_\gamma}{T}\right) \tag{9.112}$$

Next, we make use of the well-known thermodynamic relation:

$$d\left(\frac{\mu_\gamma}{T}\right) = \frac{(d\mu_\gamma)_T}{T} - \frac{h_\gamma}{T^2}\,dT \tag{9.113}$$

where the subscript (T) in the differential $d\mu_\gamma$ indicates that this differential is taken at constant temperature; h_γ is the partial specific enthalpy of component γ. Thus, the first term on the right-hand side of Eq. (9.113) expresses the change in μ_γ/T which occurs independently of the temperature, for example, as a result of the varying concentration, and the second term is exactly the temperature dependence.

For a continuous system, Eq. (9.113) assumes the following form upon division by the length element:

$$\operatorname{grad}\frac{\mu_\gamma}{T}=\frac{1}{T}(\operatorname{grad}\mu_\gamma)_T+h_\gamma\operatorname{grad}\frac{1}{T}=\frac{1}{T}(\operatorname{grad}\mu_\gamma)_T-\frac{h_\gamma}{T^2}\operatorname{grad}T \tag{9.114}$$

In connection with what has been said, Eq. (9.112) can be rewritten as

$$T\sigma_i=J_h\left(-\frac{\operatorname{grad}T}{T}\right)+\sum_\gamma\rho_\gamma\Delta_\gamma\left[F_\gamma-(\operatorname{grad}\mu_\gamma)_T\right] \tag{9.115}$$

and now the force factor corresponding to the diffusion flux $\rho_\gamma\Delta_\gamma$ in Eq. (9.112) takes the following form:

$$X_\gamma = F_\gamma - (\operatorname{grad}\mu_\gamma)_T \tag{9.116}$$

which contains no indefinite term. Let us now call the following vectorial quantity a (new) diffusion affinity of component γ:

$$A_\gamma^d=F_\gamma-(\operatorname{grad}\mu_\gamma)_T \tag{9.117}$$

Thus, in the transformation that has been just carried out we have modified the definitions of the heat flux and the diffusion affinity but the expressions for the thermal affinity and the diffusion flux remain unchanged.

Let us now consider in greater detail the application of the methods of irreversible thermodynamics to chemical reactions. Of particular interest here is the question of the applicability of linear phenomenological laws in chemical kinetics.

Let us write an elementary generalized reaction:

$$\nu_1B_1+\nu_2B_2+\ldots\underset{k'}{\overset{k}{\rightleftharpoons}}\nu_1'B_1'+\nu_2'B_2'+\ldots \tag{9.118}$$

where k and k' are the rate constants for the forward and reverse reactions. Let us agree, for a greater compactness of formulas, to designate the molar concentrations and stoichiometric coefficients of all the participants in the reaction by C_γ and ν_γ and the corresponding quantities for the reactants by C_i and ν_i and for the products by C_j and ν_j. Thus, we can write the following interrelationship:

$$\prod_\gamma C_\gamma^{\nu_\gamma}=\prod_j C_j^{\nu_j}\Big/\prod_i C_i^{\nu_i} \tag{9.119}$$

We shall now define the reaction rate by proceeding from the basic law of kinetics:

$$w_v=k\prod_i C_i^{\nu_i}-k'\prod_j C_j^{\nu_j}=\vec{w}\left(1-\lambda\prod_\gamma C_\gamma^{\nu_\gamma}\right) \tag{9.120}$$

where $\vec{w} = k \prod_i C_i^{\nu_i}$ is the rate of the forward reaction; $\lambda \equiv k'/k$. Using the van't Hoff isotherm [(5.148) through (5.152)], we write for the affinity of the reaction:

$$\mathrm{A} = -\sum_\gamma \nu_\gamma \mu_\gamma = RT \ln \frac{K_c}{\prod_\gamma C_\gamma^{\nu_\gamma}} \qquad (9.121)$$

Note here that

$$RT \ln K_c = -\sum_\gamma \nu_\gamma \mu_\gamma^\circ \qquad (9.122)$$

if μ_γ° are the chemical potentials in the standard state which depend only on the temperature for ideal gases and on the pressure too for ideal solutions.

Introducing now the affinity A from Eq. (9.121) into the rate equation, we obtain the general relationship between the reaction rate and the affinity for ideal gas mixtures and dilute solutions, this relationship being valid for any non-equilibrium state:

$$w_v = \vec{w}\left[1 - \lambda K_c \exp\left(-\frac{\mathrm{A}}{RT}\right)\right] \qquad (9.123)$$

However, on the equilibrium condition $w_v = 0$ and $\mathrm{A} = 0$ it follows from Eq. (9.123) that $k/k' = 1/\lambda = K_c$ and the rate equation assumes the form

$$w_v = \vec{w}\left[1 - \exp\left(-\frac{\mathrm{A}}{RT}\right)\right] \qquad (9.124)$$

which is also valid for any non-equilibrium state. The exponential function can be expanded into a Taylor series:

$$1 - e^{-\mathrm{A}/RT} = \frac{\mathrm{A}}{RT} - \frac{1}{2!}\left(\frac{\mathrm{A}}{RT}\right)^2 + \frac{1}{3!}\left(\frac{\mathrm{A}}{RT}\right)^3 + \ldots$$

If the reacting system is close to the state of equilibrium and the affinity is small, so that

$$\left|\frac{\mathrm{A}}{RT}\right| \ll 1 \qquad (9.125)$$

we may retain only the first term and write the reaction rate as follows:

$$w_v = \vec{w}_0 \frac{\mathrm{A}}{RT} \qquad (9.126)$$

Here, since in the Taylor series we retained only the first term, this being valid for small values of the affinity, it follows that the reaction rate $\vec{w}_0$ too refers to a point close to $w = 0$, $\mathrm{A} = 0$, i.e., to a state of equilibrium, for which reason it is denoted as $\vec{w}_0$. In other words, $\vec{w}_0$ is the rate of the forward reaction at the equilibrium state, i.e., $\vec{w}_0 = k\prod_i \bar{C}_i^{\nu_i}$, where $\bar{C}_i$ are the equilibrium concentrations of the reactants. Thus, instead of Eq. (9.124), we obtain the relation

$$w_v = \frac{\vec{w}_0}{RT} \mathrm{A} = L\mathrm{A} \tag{9.127}$$

which may be regarded as a phenomenological law of the form (9.103), which holds in this particular case for ideal gas mixtures and infinitely dilute solutions under conditions close to equilibrium. The phenomenological coefficient is defined by the relation

$$L = \vec{w}_0/RT \tag{9.128}$$

From what has been said it must be clear that the coefficient L is always positive, depends on temperature, the amount and activity of the catalyst, and is determined by the equilibrium concentrations $\bar{C}_i$ of the reactants, since these concentrations determine the rate $\vec{w}_0$. We should again emphasize the difference between $\vec{w}_0$ and the overall rate w_v (9.120), which depends on the instantaneous values of the concentrations of all the participants in the reaction.

Thus, the condition of applicability of the linear phenomenological law to chemical reactions might be thought to be the closeness to the state of equilibrium. This would, of course, impose considerable limitations on the applicability of non-equilibrium thermodynamics to chemical reactions. However, as will be shown below, the situation will not look so hopeless if the reaction may be regarded as proceeding in several elementary steps. But let us first consider the other extreme case:

$$\mathrm{A}/RT \to \infty \tag{9.129}$$

The exponent in (9.124) vanishes and $w_v = \vec{w}_0$, i.e., the rate is no longer dependent on the affinity. We may say that this corresponds to the effect of saturation with respect to the affinity, and in the region where this effect manifests itself the rate of entropy production becomes a linear function of the affinity in accordance with Eqs. (9.32) and (9.49), i.e., $T\sigma_{\text{chem}} = \mathrm{A}w_v$.

We shall now turn to the consideration of the occurrence of several reactions in a single phase. Two cases should be distinguished. In the first case, the number of elementary reactions is equal to the number of linearly independent reactions. In this case, all the relations [(9.120) through (9.127)] may be written for each of the elementary reactions and for each of them we can find the unique values of the quantities w_v, k, k', A and K_c, which are given the corresponding superscripts. In this simpler case there is no coupling between the reactions.

In the second case, the number of elementary reactions is larger than the number of linearly independent reactions, so that formally certain reaction equations can be obtained by a linear combination of other equations. Then, as is found, the relations

$$\frac{k}{k'} = K_c \quad \text{and} \quad w = \vec{w}\left[1 - \exp\left(\frac{A}{RT}\right)\right]$$

cannot be derived from the basic law of kinetics and the thermodynamic equilibrium conditions alone. In this case, as will be shown later, there appears a coupling between the reactions.

Let us return to the first case and consider first two consecutive reactions, which are expressed by linearly independent equations and, consequently, they are not coupled with each other; they are also the elementary reactions:

$$\begin{array}{ll} \text{reaction I} & B \rightleftarrows C \\ \text{reaction II} & C \rightleftarrows D \end{array} \qquad (9.130)$$

As a concrete example, let us take the following isomerization reactions:

$$o\text{-xylene} \rightleftarrows m\text{-xylene}$$

$$m\text{-xylene} \rightleftarrows p\text{-xylene}$$

Both these reactions are really reversible and have been studied in a dilute solution of xylene in toluene in the presence of $AlCl_3$ and HCl. The direct conversion o-xylene ⇄ p-xylene does not occur, therefore the linear combinations are excluded. Under conditions approaching the state of equilibrium we can write, first, the following relations for reactions (9.130):

$$\left|\frac{A_1}{RT}\right| \ll 1 \quad \text{and} \quad \left|\frac{A_2}{RT}\right| \ll 1 \qquad (9.131)$$

and, second, the phenomenological laws

$$w_1 = L_{11}A_1 \text{ and } w_2 = L_{22}A_2 \qquad (9.132)$$

Here the diagonal phenomenological coefficients

$$L_{11} = \frac{\vec{w}_{01}}{RT} \quad \text{and} \quad L_{22} = \frac{\vec{w}_{02}}{RT} \qquad (9.133)$$

contain the quantities $\vec{w}_{01}$ and $\vec{w}_{02}$, i.e., the rates of the forward elementary reactions $B \rightleftarrows C$ and $C \rightleftarrows D$ at the equilibrium state. When analysing relations (9.132) one can see that the off-diagonal coefficients are equal to zero, i.e., $L_{12} = L_{21} = 0$ and there is no coupling between reactions I and II. The situation, however, becomes different if we assume that the direct conversion $B \rightleftarrows D$ is also possible.

Let us now examine in a similar way a number of consecutive reactions according to Prigogine:

$$\begin{array}{ll} \text{reaction } 1 & B \rightleftarrows C \\ \text{reaction } 2 & C \rightleftarrows D \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \\ \text{reaction } r & X \rightleftarrows Y \end{array} \tag{9.134}$$

Assuming that the following conditions are observed:

$$\frac{A_i}{RT} \ll 1 \quad (i = 1, 2, \ldots, r) \tag{9.135}$$

we write phenomenological laws of the form (9.127):

$$w_{vi} = L_{ii}A_i \quad (i = 1, 2, \ldots, r) \tag{9.136}$$

which correspond to the general linear relations on condition that there is no coupling between the reactions, i.e., $L_{ij} = 0$ for $i \neq j$.

We can arrive at an interesting result if we dispense with the consideration of the individual elementary reactions in (9.134); let us say, they are simply unknown. Then, for the conversion

$$B \rightleftarrows Y \tag{9.137}$$

we can introduce the total affinity A and the velocity w_v. As seen from the definition of the affinity of the reaction

$$A_i = -\sum \nu_\gamma \mu_\gamma \tag{9.138}$$

the total affinity is equal to the sum of A_i for the elementary reactions:

$$A = A_1 + A_2 + \ldots + A_r \tag{9.139}$$

If the intermediate products C, D, . . ., X are unstable, say, they are free radicals and atoms, then, according to the well-known kinetic method of quasi-stationary states, we can write:

$$w_{v1} = w_{v2} = \ldots = w_{vr} = w_v \tag{9.140}$$

where w_v is the observed reaction rate. From relations (9.136) and (9.140) we obtain:

$$w_v = L_{11}A_1 = L_{22}A_2 = \ldots = L_{rr}A_r \tag{9.141}$$

Now, from Eq. (9.139) it follows that

$$A = A_1 + A_2 + \ldots + A_r = \frac{w_v}{L_{11}} + \frac{w_v}{L_{22}} + \ldots + \frac{w_v}{L_{rr}} = w_v \sum_{i=1}^{r} \frac{1}{L_{ii}} \tag{9.142}$$

If we introduce the notation

$$\sum \frac{1}{L_{ii}} = \frac{1}{L}$$

we can write:

$$w_v = L\mathrm{A} \tag{9.143}$$

Thus, the overall reaction velocity w_v measured is found to be proportional to the affinity A of reaction (9.137) and here it is essential that the relation

$$\left|\frac{\mathrm{A}}{RT}\right| \ll 1 \tag{9.144}$$

must not necessarily be satisfied provided that the conditions (9.135), namely $\mathrm{A}_i/RT \gg 1$, are observed. It has been found in practice that a large number of reactions, including catalytic reactions which proceed by a complex mechanism, follow satisfactorily the linear law (9.143). As an example, let us cite the catalytic dehydrogenation of cyclohexane or the catalytic hydrogenation of benzene in a gaseous medium: $\underset{p_1}{C_6H_{12}} \rightleftarrows \underset{p_2}{C_6H_6} + \underset{p_3}{3H_2}$, which has been studied by Prigogine, Outer and Herbo (cited from R. Haase; see the list of literature at the end of the book). In the first series of experiments (Fig. 9.4) use was made of a catalyst of the following composition (in mole per cent): 50 per cent Ni, 25 per cent ZnO, 25 per cent Cr_2O_3; the initial pressure in these experiments was the same and the temperature was varied. In the second series of experiments (Fig. 9.5) the temperature was maintained constant (548°K) and the initial partial pressures of the reactants were varied. The catalyst used for the second series had a somewhat different composition: 50 per cent Ni, 10 per cent ZnO, and 40 per cent Cr_2O_3. As can be

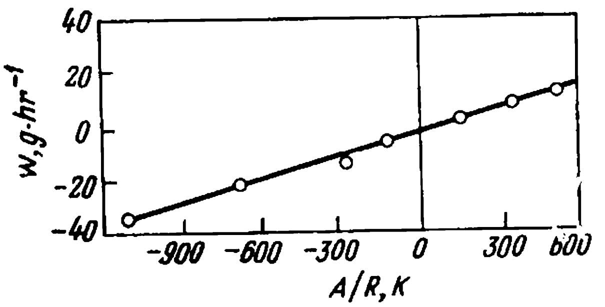


Fig. 9.4. The rate of the reaction of dehydrogenation of cyclohexane and the affinity (T ranging from 500 to 582°K):

$p_1 \times 10^{-5} = 0.0265$ N/m²; $p_2 \times 10^{-5} = 0.0990$ N/m²; $p_3 \times 10^{-5} = 0.937$ N/m²; $A/R = (-)\ 1150 - (+)\ 526$°K; $10^6\ w$ (kg/s) $= (-)\ 10 - (+)\ 3.6$.

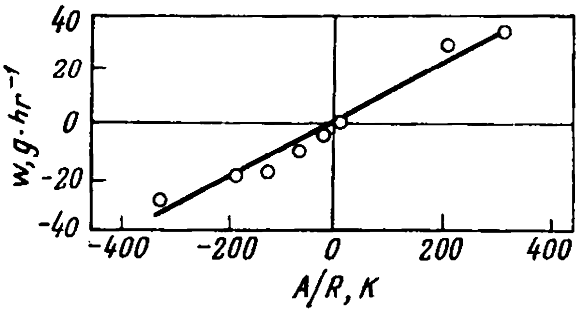
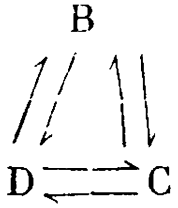


Fig. 9.5. The rate of the reaction of dehydrogenation of cyclohexane and the affinity ($T = 548$°K):

$p_1 \times 10^{-5} = 0.074 - 0.123$ N/m²; $p_2 \times 10^{-5} = 0.181 - 0.130$ N/m²; $p_3 \times 10^{-5} = 0.802 - 0.792$ N/m²; $A/R = (-)\ 197 - (+)\ 328$°K; $10^6\ w$ (kg/s) $= (-)\ 6.7 - (+)\ 0.9$.

seen from these figures, in both series of experiments, independently of the method of variation of the affinity, there was observed a linear relationship of the form (9.143). The ratios A/RT even exceeded 2, i.e., they were far from being less than unity.

We shall now consider the appearance of a coupling between two reactions, taking as an example the interconversions of the substances B, C, and D:



(9.145)

It has already been shown that in the absence of the direct conversion B ⇄ D the reactions are linearly independent and there is no coupling between them. However, the triple unimolecular reaction (9.145) may formally be described by two different methods: first, by the scheme of linearly independent reactions:

$$\begin{aligned} &\text{reaction 1} \quad \mathrm{B} \rightleftarrows \mathrm{C} \\ &\text{reaction 2} \quad \mathrm{C} \rightleftarrows \mathrm{D} \end{aligned} \tag{9.146}$$

or, second, by the scheme of linearly dependent elementary reactions:

$$\begin{array}{lll} \text{reaction I} & \mathrm{B} \rightleftarrows \mathrm{C} & \text{rate constant } k_{\mathrm{I}},\ k'_{\mathrm{I}} \\ \text{reaction II} & \mathrm{C} \rightleftarrows \mathrm{D} & k_{\mathrm{II}},\ k'_{\mathrm{II}} \\ \text{reaction III} & \mathrm{D} \rightleftarrows \mathrm{B} & k_{\mathrm{III}},\ k'_{\mathrm{III}} \end{array} \tag{9.147}$$

The first scheme (9.146) corresponds to a formal description of the macroscopic changes with the aid of mathematic mutually independent reaction equations. The second scheme (9.147) depicts the mechanism of the real elementary conversions of reacting molecules. In the second approach, as will be shown below, there appears a coupling between the reactions.

We shall first consider these consecutive reactions in the same manner as was done in discussing two consecutive uncoupled reactions. The system is assumed to be ideal, homogeneous and closed, and its volume constant. Using the label n_{γ} for the number of moles of the reactants, we write the relation between the rates according to the schemes (9.146) and (9.147):

$$-dn_{\mathrm{B}}/dt = w_1 = w_{\mathrm{I}} - w_{\mathrm{III}}; \quad -dn_{\mathrm{C}}/dt = w_2 - w_1 = w_{\mathrm{II}} - w_{\mathrm{I}};$$
$$-dn_{\mathrm{D}}/dt = -w_2 = w_{\mathrm{III}} - w_{\mathrm{II}} \tag{9.148}$$

From this it follows that

$$w_1 = w_{\mathrm{I}} - w_{\mathrm{III}} \text{ and } w_2 = w_{\mathrm{II}} - w_{\mathrm{III}} \tag{9.149}$$

We denote the chemical potential of the substance γ by μ_γ, the affinities of the general reactions by A_1 and A_2, and the affinities for the elementary reactions (9.147) by A_I, A_{II} and A_{III}. From the definition of the chemical affinity ($A = -\sum\limits_\gamma \nu_\gamma \mu_\gamma$) we find:

$$\mu_B - \mu_C = A_1 = A_I; \quad \mu_C - \mu_D = A_2 = A_{II}; \qquad (9.150)$$
$$\mu_D - \mu_B = -(A_1 + A_2) = A_{III}$$

from which we have:

$$A_I = A_1, \ A_{II} = A_2, \ A_{III} = -A_1 - A_2 \qquad (9.151)$$

For the reaction schemes (9.146) and (9.147) we can write, respectively, two series of fluxes (the reaction rates) and forces (the affinities): w_1, w_2 and A_1 and A_2, and also w_I, w_{II}, w_{III} and A_I, A_{II}, A_{III}. In going from one series of fluxes and forces to the other the rate of entropy production does not change according to Prigogine, and therefore we can write:

$$T\sigma_{\text{chem}} = w_1 A_1 + w_2 A_2 = w_I A_I + w_{II} A_{II} + w_{III} A_{III} \geqslant 0$$

At chemical equilibrium, in conformity with the well-known propositions of kinetics and thermodynamics the reaction velocities and affinities of all the linearly independent reactions become equal to zero:

$$w_1 = 0 \quad w_2 = 0 \quad \text{(equilibrium)} \qquad (9.152)$$
$$A_1 = 0 \quad A_2 = 0 \quad \text{(equilibrium)} \qquad (9.153)$$

Hence, taking cognizance of relations (9.149) and (9.151), we obtain:

$$w_I = w_{II} = w_{III} \quad \text{(equilibrium)} \qquad (9.154)$$
$$A_1 = A_{II} = A_{III} = 0 \quad \text{(equilibrium)} \qquad (9.155)$$

The conditions (9.152) and (9.154) correspond to the time independence of the numbers of moles n_B, n_C and n_D and since, by condition, the volume of the system is constant, this corresponds to the time independence of the molar concentrations of the reactants B, C and D. At the same time, in order to satisfy the general thermodynamic conditions of equilibrium it is necessary that the velocities w_I, w_{II} and w_{III} of the elementary reactions too become simultaneously equal to zero. This does not, however, follow from the relations obtained since relation (9.154) indicates only the equality of the velocities of the elementary reactions. Thus, at present we cannot yet establish phenomenological laws for states close to equilibrium on the basis of forces (affinities) and fluxes (reaction rates) assumed for three elementary reactions. And this is exactly because we do not yet know whether the velocities of elementary reactions at equilibrium vanish or not. In other words, the assumptions adopted are not sufficient and it is necessary to introduce additional considerations, which will be discussed at a later time. At this point we are interested in applications of the laws to ideal systems. Thus, for the three elementary reactions in the mechanism (9.147) we shall express the affinities through the use of the van't Hoff isotherm:

$$\mathbf{A}_{\mathrm{I}} = RT \ln \left[K_c^{\mathrm{I}} \frac{C_{\mathrm{B}}}{C_{\mathrm{C}}} \right]; \quad \mathbf{A}_{\mathrm{II}} = RT \ln \left[K_c^{\mathrm{II}} \frac{C_{\mathrm{C}}}{C_{\mathrm{D}}} \right];$$

$$\mathbf{A}_{\mathrm{III}} = RT \ln \left[K_c^{\mathrm{III}} \frac{C_{\mathrm{D}}}{C_{\mathrm{B}}} \right] \tag{9.156}$$

where the equilibrium constants K_c^i of the three elementary reactions are related to the standard chemical potentials of the reactants:

$$RT \ln K_c^{\mathrm{I}} = \mu_{\mathrm{B}}^{\circ} - \mu_{\mathrm{C}}^{\circ}; \quad RT \ln K_c^{\mathrm{II}} = \mu_{\mathrm{C}}^{\circ} - \mu_{\mathrm{D}}^{\circ};$$

$$RT \ln K_c^{\mathrm{III}} = \mu_{\mathrm{D}}^{\circ} - \mu_{\mathrm{B}}^{\circ} \tag{9.157}$$

If we denote the equilibrium concentrations by the symbol $\bar{C}_i$, we have:

$$K_c^{\mathrm{I}} = \bar{C}_{\mathrm{C}}/\bar{C}_{\mathrm{B}}; \quad K_c^{\mathrm{II}} = \bar{C}_{\mathrm{D}}/\bar{C}_{\mathrm{C}}; \quad K_c^{\mathrm{III}} = \bar{C}_{\mathrm{B}}/\bar{C}_{\mathrm{D}}$$

and

$$K_c^{\mathrm{I}} K_c^{\mathrm{II}} K_c^{\mathrm{III}} = 1 \tag{9.158}$$

The adopted condition of constant volume and the law of conservation of mass allow us to write the following relation:

$$C_{\mathrm{B}} + C_{\mathrm{C}} + C_{\mathrm{D}} = \bar{C}_{\mathrm{B}} + \bar{C}_{\mathrm{C}} + \bar{C}_{\mathrm{D}} \tag{9.159}$$

Thus, we have three independent equations which give the equilibrium concentrations $\bar{C}_B$, $\bar{C}_C$, $\bar{C}_D$. Let us now apply the basic law of kinetics to the three elementary reactions I, II, III (9.147):

$$\begin{aligned} w_{\mathrm{I}} &= k_{\mathrm{I}} C_{\mathrm{B}}^{1} - k'_{\mathrm{I}} C_{\mathrm{C}} = \vec{w}_{\mathrm{I}} \left(1 - \lambda_{\mathrm{I}} \frac{C_{\mathrm{C}}}{C_{\mathrm{B}}} \right) \\ w_{\mathrm{II}} &= k_{\mathrm{II}} C_{\mathrm{C}} - k'_{\mathrm{II}} C_{\mathrm{D}} = \vec{w}_{\mathrm{II}} \left(1 - \lambda_{\mathrm{II}} \frac{C_{\mathrm{D}}}{C_{\mathrm{C}}} \right) \\ w_{\mathrm{III}} &= k_{\mathrm{III}} C_{\mathrm{D}} - k'_{\mathrm{III}} C_{\mathrm{B}} = \vec{w}_{\mathrm{III}} \left(1 - \lambda_{\mathrm{III}} \frac{C_{\mathrm{B}}}{C_{\mathrm{D}}} \right) \end{aligned} \tag{9.160}$$

where

$$\vec{w}_{\mathrm{I}} \equiv k_{\mathrm{I}} C_{\mathrm{B}}, \quad \vec{w}_{\mathrm{II}} \equiv k_{\mathrm{II}} C_{\mathrm{C}}, \quad \vec{w}_{\mathrm{III}} \equiv k_{\mathrm{III}} C_{\mathrm{D}} \tag{9.161}$$

and

$$\lambda_{\mathrm{I}} = \frac{k'_{\mathrm{I}}}{k_{\mathrm{I}}}, \quad \lambda_{\mathrm{II}} = \frac{k'_{\mathrm{II}}}{k_{\mathrm{II}}}, \quad \lambda_{\mathrm{III}} = \frac{k'_{\mathrm{III}}}{k_{\mathrm{III}}} \tag{9.162}$$

In accordance with the symbols in the scheme (9.147), k_i and k'_i are the rate constants of the forward and reverse reactions, respectively, while $\overrightarrow{w}_i$ are the rates of the elementary reactions that proceed from left to right, i.e., they are forward reactions. Substituting expressions (9.156) into Eq. (9.160), we obtain the general relationship between the velocities of the reactions and their affinities:

$$\begin{aligned} w_{\mathrm{I}} &= \overrightarrow{w}_{\mathrm{I}}\,[1-\lambda_{\mathrm{I}}K_c^{\mathrm{I}}\exp(-\mathrm{A}_{\mathrm{I}}/RT)] \\ w_{\mathrm{II}} &= \overrightarrow{w}_{\mathrm{II}}\,[1-\lambda_{\mathrm{II}}K_c^{\mathrm{II}}\exp(-\mathrm{A}_{\mathrm{II}}/RT)] \\ w_{\mathrm{III}} &= \overrightarrow{w}_{\mathrm{III}}\,[1-\lambda_{\mathrm{III}}K_c^{\mathrm{III}}\exp(-\mathrm{A}_{\mathrm{III}}/RT)] \end{aligned} \tag{9.163}$$

These relations hold for any departure from the state of equilibrium in ideal systems (ideal gases, infinitely dilute solutions). From the equilibrium conditions (9.154) and (9.155), on the basis of Eq. (9.163), we obtain:

$$\overrightarrow{w}_{0\mathrm{I}}\,(1-\lambda_{\mathrm{I}}K_c^{\mathrm{I}}) = \overrightarrow{w}_{0\mathrm{II}}\,(1-\lambda_{\mathrm{II}}K_c^{\mathrm{II}}) = \overrightarrow{w}_{0\mathrm{III}}\,(1-\lambda_{\mathrm{III}}K_c^{\mathrm{III}}) \tag{9.164}$$

Here $\overrightarrow{w}_{0i}$ are the velocities of the forward reactions at equilibrium, i.e.,

$$\overrightarrow{w}_{0\mathrm{I}} = k_{\mathrm{I}}\bar{C}_{\mathrm{B}}; \quad \overrightarrow{w}_{0\mathrm{II}} = k_{\mathrm{II}}\bar{C}_{\mathrm{C}}; \quad \overrightarrow{w}_{0\mathrm{III}} = k_{\mathrm{III}}\bar{C}_{\mathrm{D}} \tag{9.165}$$

All these formulas have been obtained from the conditions of chemical equilibrium and the laws of chemical kinetics. In this derivation, on the basis of equality (9.154), $w_{\mathrm{I}} = w_{\mathrm{II}} = w_{\mathrm{III}}$ at equilibrium, one could have arrived at the conclusion that the cyclic occurrence of the reactions under equilibrium conditions is possible:

$$\begin{tikzcd} & \mathrm{B} \arrow[dr] & \\ \mathrm{C} \arrow[ur] & & \mathrm{D} \arrow[ll] \end{tikzcd} \tag{9.166}$$

However, on the whole the results obtained are found to be unsatisfactory, and the scheme (9.166) given above cannot be realized under equilibrium conditions. For the subsequent discussion we have to resort to the *principle of detailed balance* (Fowler, 1929), which is special case of the principle of microscopic reversibility (Tolman, 1924). According to these principles in an equilibrium system any elementary process occurs at the same rate in both directions. In the case under consideration the result is that the rates of the elementary reactions are not only equal, as stated in Eq. (9.154), but each of them is equal to zero, i.e.,

$$w_{\mathrm{I}} = 0, \quad w_{\mathrm{II}} = 0, \quad w_{\mathrm{III}} = 0 \tag{9.167}$$

Thus the principle of detailed balance excludes the cyclic conversion (9.166) and is complementary to relation (9.154). From formulas (9.163) and (9.167) and also from (9.155) it follows that

$$\lambda_{\mathrm{I}} K_c^{\mathrm{I}} = \lambda_{\mathrm{II}} K_c^{\mathrm{II}} = \lambda_{\mathrm{III}} K_c^{\mathrm{III}} = 1 \qquad (9.168)$$

or, with account taken of Eq. (9.168),

$$K_c^{\mathrm{I}} = \frac{k_{\mathrm{I}}}{k'_{\mathrm{I}}}, \quad K_c^{\mathrm{II}} = \frac{k_{\mathrm{II}}}{k'_{\mathrm{II}}}, \quad K_c^{\mathrm{III}} = \frac{k_{\mathrm{III}}}{k'_{\mathrm{III}}} \qquad (9.169)$$

It should be noted that in the case of coupled reactions expressions (9.169) are obtained only with the aid of the principle of detailed balance; otherwise they are found only from the thermodynamic equilibrium conditions and the laws of chemical kinetics. From relations (9.163) and (9.168) we find that

$$\begin{aligned} w_{\mathrm{I}} &= \overrightarrow{w}_{\mathrm{I}} [1 - \exp(-\mathrm{A}_{\mathrm{I}}/RT)] \\ w_{\mathrm{II}} &= \overrightarrow{w}_{\mathrm{II}} [1 - \exp[-\mathrm{A}_{\mathrm{II}}/RT)] \\ w_{\mathrm{III}} &= \overrightarrow{w}_{\mathrm{III}} [1 - \exp(-\mathrm{A}_{\mathrm{III}}/RT)] \end{aligned} \qquad (9.170)$$

Turning to states close to a state of equilibrium, we shall assume that the following relations are fulfilled:

$$\left|\frac{\mathrm{A}_{\mathrm{I}}}{RT}\right| \ll 1, \quad \left|\frac{\mathrm{A}_{\mathrm{II}}}{RT}\right| \ll 1, \quad \left|\frac{\mathrm{A}_{\mathrm{III}}}{RT}\right| \ll 1 \qquad (9.171)$$

and accordingly, expanding the exponential functions (9.170) into a series and retaining only the first terms, we write:

$$w_{\mathrm{I}} = \frac{\overrightarrow{w}_{0\mathrm{I}}}{RT} \mathrm{A}_{\mathrm{I}}; \quad w_{\mathrm{II}} = \frac{\overrightarrow{w}_{0\mathrm{II}}}{RT} \mathrm{A}_{\mathrm{II}}; \quad w_{\mathrm{III}} = \frac{\overrightarrow{w}_{0\mathrm{III}}}{RT} \mathrm{A}_{\mathrm{III}} \qquad (9.172)$$

On the other hand, for the rates w_1 and w_2 and the affinities A_1 and A_2 of the general linearly independent reactions (1) and (2) in the scheme (9.146) we obtain the following expressions on the basis of relations (9.172), (9.149) and (9.151):

$$w_1 = \frac{\overrightarrow{w}_{0\mathrm{I}} + \overrightarrow{w}_{0\mathrm{III}}}{RT} \mathrm{A}_1 + \frac{\overrightarrow{w}_{0\mathrm{III}}}{RT} \mathrm{A}_2 \qquad (9.173)$$

$$w_2 = \frac{\overrightarrow{w}_{0\mathrm{III}}}{RT} \mathrm{A}_1 + \frac{\overrightarrow{w}_{0\mathrm{II}} + \overrightarrow{w}_{0\mathrm{III}}}{RT} \mathrm{A}_2 \qquad (9.174)$$

which have the common form of phenomenological laws:

$$w_1 = L_{11}\mathrm{A}_1 + L_{12}\mathrm{A}_2 \text{ and } w_2 = L_{21}\mathrm{A}_1 + L_{22}\mathrm{A}_2 \qquad (9.175)$$

Here the Onsager reciprocal relation is fulfilled:

$$L_{12} = L_{21} \qquad (9.176)$$

The values of the phenomenological off-diagonal coefficients L_{ik} $(i, k = 1, 2)$ are determined by comparing Eqs. (9.173), (9.174) and (9.175):

$$L_{11}=\frac{\vec{w}_{0\mathrm{I}}+\vec{w}_{0\mathrm{III}}}{RT};\quad L_{12}=L_{21}=\frac{\vec{w}_{0\mathrm{III}}}{RT};\quad L_{22}=\frac{\vec{w}_{0\mathrm{II}}+\vec{w}_{0\mathrm{III}}}{RT}$$

Thus, reactions (1) and (2) are found to be coupled through the off-diagonal coefficients, which are in this case different from zero. An essential point is that the Onsager fundamental theorem, which finds expression in a special statement (9.176), stems directly from the principle of detailed balance (or, more generally, from the principle of microscopic reversibility). This conclusion was made by Onsager.

9.12. Relaxation Processes and the Relaxation Time

An important part in the behaviour of physico-chemical systems is played by *relaxation processes*, which bring the system to a state of equilibrium. If an equilibrium system is acted on by an external force, even for a short time, say it is compressed or subjected to an electric or light impact, then such a system can be switched out of the state of initial equilibrium. If the external factor that caused the shift disappears, the system will tend to return at a certain rate to the initial equilibrium state—this is what we call the relaxation. On the other hand, if the external force operates for a long time, creating new conditions for the existence of the system, then to these conditions there will correspond a new different equilibrium state. The transition to this new state will also be taken place in time—this is also a relaxation process. Since any chemical change leads the system to a state of equilibrium, it follows that any chemical reaction may be regarded as a relaxation process. Many methods have been developed for the study of the rates of chemical reactions; they are known as relaxation methods. As an example may be cited the study of the recombination of iodide ions in solution. A solution of iodine in carbon tetrachloride, for example, is illuminated by a flash of light of short duration. This causes the iodine molecules to dissociate into free atoms, which, unlike the molecules, do not absorb visible light. It is for this reason that the recombination of atoms (i.e., a relaxation process) into molecules can be followed by measuring the density of the solution. Local relaxation processes occur constantly in the case of various types of fluctuations and also, for example, during the passage of sound through a medium, which is evidently associated with local adiabatic compressions.

Let us first consider the relaxation process and define the concept of the relaxation time with the aid of the methods of chemical kinetics. The rate of reaction r for any system is known to be determined as $w_r = d\xi_r/dt$. Here the extent of reaction—the chemical variable ξ_r—may be considered to be an independent variable and, accordingly, the reaction rate w_r may be defined as a derivative of the properties of the system (the state parameters) with respect to time t only for closed systems with linearly independent reactions. For open systems and linearly dependent reactions the change of the mass (the number of moles) of a substance can occur in several ways, in which various changes in the extent of reaction correspond to the individual elementary reactions. In what follows the extent of reaction ξ_r may be assumed to be a function of time t; we shall deal only with closed systems and assume that the reaction equations may be written so that they correspond to linearly independent reactions. Let us take a single reaction (the chemical variable ξ and the affinity A) which takes place in a closed phase,

$$\mathrm{B} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{C}$$

We assume that the reaction is first-order in both directions and that at time zero the system consists only of substance B and therefore the concentrations of B and C are proportional, respectively, to $1-\xi$ and ξ, where ξ, as before, is the extent of reaction (a chemical variable). We also assume that by the time of our observation ($t=0$) the system has been changed and the chemical variable ξ has reached the value ξ_0. The reaction rate at a given instant of time will be given by

$$w=\frac{d\xi}{dt}=k(1-\xi)-k'\xi=k-k\xi-k'\xi=(k+k')\left(\frac{k}{k+k'}-\xi\right) \tag{9.177}$$

At equilibrium the rate vanishes and therefore the ratio of the rate constants $k/(k+k')=\bar{\xi}$, i.e., is the equilibrium value of the extent of reaction. Thus, Eq. (9.177) reduces to the following equation:

$$\frac{d\xi}{\bar{\xi}-\xi}=(k+k')\,dt \tag{9.178}$$

Integrating Eq. (9.178) from $t=0$ to t and from ξ_0 to ξ, we obtain:

$$\frac{\xi-\bar{\xi}}{\xi_0-\bar{\xi}}=e^{-(k+k')t} \tag{9.179}$$

We introduce a certain time τ, defined by the relation $\tau=1/(k+k')$ and call it the *relaxation time*. From Eq. (9.179) it follows that at $t=\tau$

$$\frac{\xi-\bar{\xi}}{\xi_0-\bar{\xi}}=e^{-1}=\frac{1}{e} \tag{9.180}$$

The difference $\xi-\bar{\xi}$ may be called a departure from the equilibrium state. Therefore, for the time period equal to the relaxation time the departure from the state of equilibrium diminishes e times. This may be taken as the definition of the relaxation time. For further comparisons, we shall simplify the form of Eq. (9.179) by making the substitution $C = \xi_0 - \bar{\xi}$, i.e.,

$$\xi = \bar{\xi} + Ce^{-t/\tau} \tag{9.181}$$

In studying the kinetics of chemical reactions it is customary practice to keep constant some of the properties (temperature and volume, temperature and pressure, etc.). Therefore, strictly speaking, both the equilibrium extent of reaction and the relaxation time should be labelled with subscripts, ξ_{xy} and τ_{xy}, where x and y are the properties of the system (its state parameters), which remain constant. This is what we are going to do, but with the aid of thermodynamics. Let us consider a phenomenological law that has been derived earlier for near-equilibrium conditions:

$$w = \frac{d\xi}{dt} = L\mathbf{A} \tag{9.182}$$

where L is the phenomenological coefficient. Since the system is closed by condition, the affinity $\mathbf{A}$ depends on the chemical variable ξ and at $\xi = \bar{\xi}$ it turns to zero. Besides, since the chemical affinity is a property of the system, it may be regarded as being a function of other variables that define the state of the system. On the whole, for a homogeneous closed system it will be reasonable to consider the affinity to be additionally dependent on the following pairs of variables: temperature and pressure, temperature and volume, entropy and pressure, entropy and volume. In other words, we can write in general form the following dependences:

$$\begin{aligned} &\mathbf{A} = \mathbf{A}\,(T,\ p,\ \xi); \qquad \mathbf{A} = \mathbf{A}\,(T,\ v,\ \xi); \\ &\mathbf{A} = \mathbf{A}\,(S,\ p,\ \xi); \qquad \mathbf{A} = \mathbf{A}\,(S,\ v,\ \xi) \end{aligned} \tag{9.183}$$

Further in the text, in order to make use of the phenomenological law (9.182) we should establish the dependence $\mathbf{A} = \mathbf{A}(\xi)$. Unfortunately, this dependence has not been found in a general form. Therefore, first, assuming that the two properties chosen remain constant, the chemical affinity $\mathbf{A}$ is taken to be dependent only on ξ. Second, we expand the function $\mathbf{A} = \mathbf{A}(\xi)$ into a series and since we have adopted in Eq. (9.182) that the system is close to the state of equilibrium, we retain only the first term in the expansion. The result is

$$\mathbf{A} = \left(\frac{\partial \mathbf{A}}{\partial \xi}\right)_{x,\,y} (\xi - \bar{\xi}) \tag{9.184}$$

Here the partial derivative must be evaluated with the adopted conditions remaining constant in accordance with Eq. (9.183).

From relations (9.182) and (9.184) we find:

$$\frac{d\xi}{dt} = L\left(\frac{\partial A}{\partial \xi}\right)_{x,\,y}(\xi - \bar{\xi}) \tag{9.185}$$

Here, in accordance with Eq. (9.183), i.e., with the choice of a pair of the properties of the system that remain constant, we have four equations of the form (9.185). In these equations the phenomenological coefficient L has a common value if the system under consideration has the same initial temperature and pressure and, by condition, is not far removed from equilibrium. On the contrary, the four partial derivatives

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,\,p},\quad \left(\frac{\partial A}{\partial \xi}\right)_{T,\,v},\quad \left(\frac{\partial A}{\partial \xi}\right)_{S,\,p},\quad \left(\frac{\partial A}{\partial \xi}\right)_{S,\,v} \tag{9.186}$$

differ from one another in a general case. Using these derivatives, we can formulate the conditions of the stability of the equilibrium state of a chemical system:

$$\frac{\partial A}{\partial \xi} < 0 \tag{9.187}$$

that is, at equilibrium the chemical affinity must diminish at a possible, let us say, random variation of ξ (the fluctuations do not bring the system out of the equilibrium state). On the other hand, the diagonal phenomenological coefficient L is positive at all times, as follows from Eq. (9.182):

$$L > 0 \tag{9.188}$$

Introducing the abbreviated notations

$$\tau_{x,\,y} = -\frac{1}{L}\left(\frac{\partial \xi}{\partial A}\right)_{x,\,y}$$

or, separately for the four combinations of the constant properties,

$$\begin{aligned} \tau_{T,\,p} &= -\frac{1}{L}\left(\frac{\partial \xi}{\partial A}\right)_{T,\,p}; \quad \tau_{T,\,v} = -\frac{1}{L}\left(\frac{\partial \xi}{\partial A}\right)_{T,\,v} \\ \tau_{S,\,p} &= -\frac{1}{L}\left(\frac{\partial \xi}{\partial A}\right)_{S,\,p}; \quad \tau_{S,\,v} = -\frac{1}{L}\left(\frac{\partial \xi}{\partial A}\right)_{S,\,v} \end{aligned} \tag{9.189}$$

we integrate under these conditions Eqs. (9.185) separately for each of the four cases. The result is

$$\frac{d\xi}{\xi - \bar{\xi}} = -\frac{1}{\tau_{x,\,y}}\,dt; \qquad -\ln(\xi - \bar{\xi}) = \frac{1}{\tau_{x,\,y}} + \ln C$$

and, in accordance with Eq. (9.189), we can write four equations:

$$\begin{aligned} \xi(t) &= \bar{\xi}_{(T,\,p)} + C_1 e^{-t/\tau_{T,\,p}}; \quad \xi(t) = \bar{\xi}_{(T,\,v)} + C_2 e^{-t/\tau_{T,\,v}} \\ \xi(t) &= \bar{\xi}_{(S,\,p)} + C_3 e^{-t/\tau_{S,\,p}}; \quad \xi(t) = \bar{\xi}_{(S,\,v)} + C_4 e^{-t/\tau_{S,\,v}} \end{aligned} \tag{9.190}$$

where C_1, C_2, C_3, C_4 are the integration constants. Relations (9.190) have the form of the kinetic equation (9.181) and the four quantities $\tau_{T,p}$, $\tau_{T,v}$, $\tau_{S,p}$, $\tau_{S,v}$ are the relaxation times for different conditions of existence of the system which are defined by the constancy of the pair of variables chosen. Taking cognizance of relations (9.187), (9.189) and (9.190), we find that all the values of τ are positive, i.e.,

$$\tau_{x,y} > 0 \tag{9.191}$$

Let us now find the relationship between the four values of relaxation time on the basis of the definitions (9.189) and thermodynamic rearrangements:

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,v} = \left(\frac{\partial A}{\partial \xi}\right)_{T,p} + \left(\frac{\partial A}{\partial p}\right)_{T,\xi}\left(\frac{\partial p}{\partial \xi}\right)_{T,v} \tag{9.192}$$

$$\left(\frac{\partial v}{\partial \xi}\right)_{T,p} = -\left(\frac{\partial p}{\partial \xi}\right)_{T,v}\left(\frac{\partial v}{\partial p}\right)_{T,\xi} \tag{9.193}$$

and also the well-known dependence

$$\left(\frac{\partial A}{\partial p}\right)_{T,\xi} = -\left(\frac{\partial v}{\partial \xi}\right)_{T,p} \tag{9.194}$$

Let us now determine the isobaric-isothermal change of the volume as a result of the reaction,

$$v_{T,p} = \left(\frac{\partial v}{\partial \xi}\right)_{T,p}$$

and the isothermal compressibility

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,\xi} > 0$$

From these relations and also from Eq. (9.187) and the notations in (9.189) it follows that

$$\frac{\tau_{T,p}}{\tau_{T,v}} = \frac{\left(\frac{\partial \xi}{\partial A}\right)_{T,p}}{\left(\frac{\partial \xi}{\partial A}\right)_{T,v}} = 1 - \frac{(v_{T,p})^2}{\beta_T v}\left(\frac{\partial \xi}{\partial A}\right)_{T,p} \geqslant 1 \tag{9.195}$$

Here the equality holds for a special case when the volume of the system does not change during the course of the reaction. Let us write the following identities:

$$\left(\frac{\partial A}{\partial \xi}\right)_{S,v} = \left(\frac{\partial A}{\partial \xi}\right)_{S,p} + \left(\frac{\partial A}{\partial p}\right)_{S,\xi}\left(\frac{\partial p}{\partial \xi}\right)_{S,v}$$

$$\left(\frac{\partial v}{\partial \xi}\right)_{S,p} = -\left(\frac{\partial p}{\partial \xi}\right)_{S,v}\left(\frac{\partial v}{\partial p}\right)_{S,\xi}$$

and also the well-known dependence

$$\left(\frac{\partial A}{\partial p}\right)_{S,\xi} = -\left(\frac{\partial v}{\partial \xi}\right)_{S,p}$$

We make use of the definition of the volume change arising from the reaction at constant entropy and pressure:

$$v_{S,\,p} \equiv \left(\frac{\partial v}{\partial \xi}\right)_{S,\,p}$$

and the expression for the adiabatic compressibility

$$\beta_S = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{S,\,\xi} > 0$$

From this, with account taken of Eq. (9.187) and also of (9.180), we obtain:

$$\frac{\tau_{S,\,p}}{\tau_{S,\,v}} = 1 - \frac{(v_{S,\,p})^2}{\beta_S v}\left(\frac{\partial \xi}{\partial A}\right)_{S,\,p} \geqslant 1 \tag{9.196}$$

We may also write the following equalities:

$$\left(\frac{\partial A}{\partial \xi}\right)_{S,\,v} = \left(\frac{\partial A}{\partial \xi}\right)_{T,\,v} + \left(\frac{\partial A}{\partial T}\right)_{v,\,\xi}\left(\frac{\partial T}{\partial \xi}\right)_{S,\,v}$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,\,v} = -\left(\frac{\partial T}{\partial \xi}\right)_{S,\,v}\left(\frac{\partial S}{\partial T}\right)_{v,\,\xi}$$

and the following relationship:

$$\left(\frac{\partial A}{\partial T}\right)_{v,\,\xi} = \left(\frac{\partial S}{\partial \xi}\right)_{T,\,v}$$

We also introduce the entropy change of the reaction, which takes place at constant temperature and volume

$$S_{T,\,v} = \left(\frac{\partial S}{\partial \xi}\right)_{T,\,v}$$

and define the constant-volume heat capacity in terms of the entropy:

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_{v,\,\xi} > 0$$

Next, taking cognizance of formulas (9.187) and (9.189), we get:

$$\frac{\tau_{T,\,v}}{\tau_{S,\,v}} = 1 - \frac{T\,(S_{T,\,v})^2}{C_v}\left(\frac{\partial \xi}{\partial A}\right)_{T,\,v} \geqslant 1 \tag{9.197}$$

where the equality applies to a special case where the entropy does not change (i.e., $S_{T,\,v} = 0$) when the reaction proceeds at constant temperature and volume.

Finally, let us consider the following identities:

$$\left(\frac{\partial A}{\partial \xi}\right)_{S,\,p} = \left(\frac{\partial A}{\partial \xi}\right)_{T,\,p} + \left(\frac{\partial A}{\partial T}\right)_{p,\,\xi}\left(\frac{\partial T}{\partial \xi}\right)_{S,\,p}$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,\,p} = -\left(\frac{\partial T}{\partial \xi}\right)_{S,\,p}\left(\frac{\partial S}{\partial T}\right)_{p,\,\xi}$$

and the relationship

$$\left(\frac{\partial \mathbf{A}}{\partial T}\right)_{p,\,\xi}=\left(\frac{\partial S}{\partial \xi}\right)_{T,\,p}$$

We now introduce the entropy change for an isobaric-isothermal reaction:

$$S_{T,\,p}\equiv\left(\frac{\partial S}{\partial \xi}\right)_{T,\,p}$$

and define the constant-pressure heat capacity in terms of the entropy:

$$C_p=T\left(\frac{\partial S}{\partial T}\right)_{p,\,\xi}>0$$

Now, in the light of Eqs. (9.187) and (9.189), we have:

$$\frac{\tau_{T,\,p}}{\tau_{S,\,p}}=1-\frac{T\,(S_{T,\,p})^2}{C_p}\left(\frac{\partial \xi}{\partial \mathbf{A}}\right)_{T,\,p}\geqslant 1 \qquad (9.198)$$

where the equality holds for the special case $S_{T,p}=0$. The thermodynamic quantities in formulas (9.195), (9.196), (9.197) and (9.198) always refer to equilibrium conditions ($\mathbf{A}=0$, $\xi=\bar{\xi}$). From this it follows that the reaction entropy $S_{T,\,p}$ in Eq. (9.198) is connected with the reaction enthalpy $h_{T,\,p}$:$h_{T,\,p}=TS_{T,\,p}$. Hence, the special case $S_{T,\,p}=0$ corresponds to a thermally neutral reaction. The simultaneous solution of Eqs. (9.195), (9.196), (9.197) and (9.198) leads to the following inequalities:

$$\tau_{T,\,p}\geqslant\tau_{T,\,v}\geqslant\tau_{S,\,v} \quad \text{and} \quad \tau_{T,\,p}\geqslant\tau_{S,\,p}\geqslant\tau_{S,\,v} \qquad (9.199)$$

These inequalities are reminiscent of the classical conditions of the stability of the system: $C_p > C_v$; $\beta_T > \beta_S$. It may be pointed out that relaxation processes account for the various *after-effect* phenomena observed, for example, in glasses (or in other materials in the vitreous state). These phenomena cannot be explained within the framework of classical thermodynamics since at a given temperature and pressure and also at constant mass and unchanged composition the state of the system is not defined unambiguously. Thus, for example, with the lapse of time in such a system the volume, the refractive index or any other property are changed. In such cases one speaks of after-effect phenomena; they occur in frozen systems. Such phases are in fact nonequilibrium phases and differ in this respect from ordinary liquids, well heated crystals, also from gases, i.e., systems that are at internal equilibrium. The after-effect phenomena are caused by internal transformations that occur in the system in the direction of the equilibrium state, i.e., by relaxation.

9.13. Stationary States in Continuous Systems. The Glansdorf-Prigogine Theorem

The stationary states, states in which the properties of a system are time-independent, play an important part in applications of nonequilibrium (irreversible) thermodynamics, especially in biology. Stationary nonequilibrium states have a special important feature: under certain conditions they are characterized by a minimum rate of entropy production, which is compatible with the external restraints imposed on the system. This feature manifests itself under the conditions of constant phenomenological coefficients. Since this is generally not valid for real systems, what has just been said means that the overall gradients of the thermodynamic properties throughout the entire system must be small enough for the assumption of constant phenomenological coefficients to be approximately justified.

The well-known Glansdorf-Prigogine theorem (1970) on the minimum rate of entropy production states: In any closed or open system that obeys the Onsager reciprocal relations, where the macroscopic rate is equal to zero and the local values of the properties T, $\mu_1, \ldots, \mu_n$ are fixed at boundary surfaces, the stationary state ($\partial T/\partial t = 0$, $\partial \mu_\gamma/\partial t = 0$ at every point) corresponds to the minimum of the function $\theta \equiv \int\limits_v \sigma_S \, \delta v$ — the rate of entropy production throughout the entire system.

During the evolution of the system from the initial state to its stationary state the rate of entropy production ($\partial\theta/\partial t$) constantly diminishes:

$$\frac{\partial \theta}{\partial t} = \int\limits_v \frac{\partial \sigma_S}{\partial t} \, \delta v = \int\limits_v \sum_i \left(J_i \frac{\partial X_i}{\partial t} + X_i \frac{\partial J_i}{\partial t} \right) \delta v < 0 \qquad (9.200)$$

In a stationary state the change of the rate (acceleration) of entropy production in the system is stopped and

$$\frac{\partial \theta}{\partial t} = 0 \qquad (9.201)$$

But if the Onsager conditions are not fulfilled, the theorem (9.200) cannot be proved in a general form. However, according to Glansdorf and Prigogine (1954), one can derive an inequality that includes the changes of only the forces with time but not of the fluxes:

$$\int\limits_v \sum_i J_i \frac{\partial X_i}{\partial t} \, \delta v < 0 \qquad (9.202)$$

This relation has been applied to the study of the evolution of the system in the nonlinear region and also of the cyclic evolutions near the stationary state (Prigogine and Belescu, 1955-1956).

We shall now turn to the consideration of some concrete problems associated with transport processes.

9.14. Diffusion in Isothermal Systems

Let us first write the equation for the Gibbs free energy per unit volume of the system:

$$\delta g_v = -S_v \delta T + \delta p + \sum_\gamma \mu_\gamma \delta C_\gamma \tag{9.203}$$

Here the differentials imply the applicability of the equation to open systems; the variations of the concentrations are associated with the change in the number of moles $\delta C_\gamma = \delta n_\gamma / v$, where δn_γ may have quite arbitrary values and are the possible or actual changes in the number of moles n_γ. Integrating* Eq. (9.203) at constant T, p and μ_γ with the change of g_v from 0 to g_v and of C_γ from 0 to C_γ, we obtain:

$$g_v = \sum_\gamma \mu_\gamma C_\gamma \tag{9.204}$$

Differentiating again and comparing the differentials from Eq. (9.203), we arrive at the relation

$$\delta p = S_v \, dT + \sum_\gamma C_\gamma \, \delta \mu_\gamma$$

which is called the Gibbs-Duhem equation in a local form. If the temperature is assumed to be constant, we can write $\delta p = \sum_\gamma C_\gamma \delta \mu_\gamma$ or, for a system with the continuously changing variables along the line of motion,

$$\operatorname{grad} p = \sum_\gamma C_\gamma \operatorname{grad} \mu_\gamma \tag{9.205}$$

Let us further agree to examine the problem of the rate of diffusion in unaccelerated and nonviscous liquids. In this case Eq. (9.80) leads to the following:

$$\operatorname{grad} p = \sum_\gamma \rho_\gamma F_\gamma = \sum_\gamma C_\gamma F_\gamma^* \tag{9.206}$$

where we introduced an additional external force which acts on one mole of component γ: $F_\gamma^* = M_\gamma F_\gamma$. From Eqs. (9.205) and

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* Here g_v is assumed to be a homogeneous function of the first degree.

(9.206) it follows that

$$\sum_{\gamma} C_{\gamma} \operatorname{grad} \mu_{\gamma} = \sum_{\gamma} C_{\gamma} F_{\gamma}^{*} \tag{9.207}$$

Next we shall consider a two-component system. The rate of production of entropy arising in such a system from diffusion may be written, on the basis of Eq. (9.115) and assuming that grad $T = 0$ by condition, as follows:

$$T\sigma_{\text{diff}} = \rho_1 \Delta_1 [F_1 - (\operatorname{grad} \mu_1)_T] + \rho_2 \Delta_2 [F_2 - (\operatorname{grad} \mu_2)_T] \geqslant 0$$

or, introducing the molar concentration instead of the mass of the component per unit volume with the aid of the relation $\rho_{\gamma} = C_{\gamma} M_{\gamma}$, we shall have:

$$T\sigma_{\text{diff}} = C_1 \Delta_1 [F_1^* - (\operatorname{grad} \mu_1)_T] + C_2 \Delta_2 [F_2^* - (\operatorname{grad} \mu_2)_T] = \\ = C_1 \Delta_1 \mathbf{A}_1^{*d} + C_2 \Delta_2 \mathbf{A}_2^{*d} \geqslant 0 \tag{9.208}$$

where

$$\mathbf{A}_{\gamma}^{*d} = F_{\gamma}^{*} - (\operatorname{grad} \mu_{\gamma}^{*})_T \tag{9.209}$$

is a new expression for the diffusion affinity. It may also be noted that in the last transformations the chemical potential is converted from a specific to a molar quantity. From Eqs. (9.207) and (9.209) we obtain the following general relationship for diffusion:

$$\sum_{\gamma} C_{\gamma} \mathbf{A}_{\gamma}^{*d} = 0 \tag{9.210}$$

In particular, for a two-component system

$$\mathbf{A}_2^{*d} = -\frac{C_1}{C_2} \mathbf{A}_1^{*d} \tag{9.211}$$

According to relation (9.67), which connects the rates of diffusion of the individual components, $\sum \rho_{\gamma} \Delta_{\gamma} = 0$,

$$C_2 M_2 \Delta_2 = -C_1 M_1 \Delta_1 \tag{9.212}$$

and also Eqs. (9.208) and (9.211) lead to the expression for the rate of diffusion production of entropy in an isothermal medium:

$$T\sigma_{\text{diff}} = \left(1 + \frac{C_1 M_1}{C_2 M_2}\right) C_1 \Delta_1 \mathbf{A}_1^{*d} \geqslant 0 \tag{9.213}$$

This relation shows that in a binary system there is really only one diffusional flux. In the region of small values of the diffusion affinity $\mathbf{A}_1^{*d}$ the flux may be expected to obey the proportionality relation:

$$\left(1 + \frac{C_1 M_1}{C_2 M_2}\right) C_1 \Delta_1 = L_{11} \mathbf{A}^{*d} \tag{9.214}$$

In the absence of noticeable external forces [when, according to Eq. (9.209), $\mathbf{A}_{\gamma}^{*d} = -(\operatorname{grad} \mu_{\gamma})_T$] and on the condition that in solution $C_1M_1 \ll C_2M_2$, Eq. (9.214) changes to the following expression:

$$C_1\Delta_1 = -L_{11} (\text{grad } \mu_1)_T \tag{9.215}$$

For perfect (or ideal) solutions $\mu = \mu^\circ + RT \ln C$ and grad $\mu = RT$ grad $\ln C = RT\,(1/C)$ grad C, and then

$$C_1\Delta_1 = -L_{11} \frac{RT}{C_1} \text{grad } C_1 \tag{9.216}$$

If component *1* is regarded as a solute contained in a small concentration in solvent *2*, whose rate of diffusion Δ_2 practically coincides with the rate of diffusion of the centre of mass ω (9.66), then formula (9.216) is identified with Fick's law:

$$C_1\Delta_1 = -D_1 \text{ grad } C_1 \tag{9.217}$$

in which the diffusion coefficient D_1 remains constant in the region of concentrations at which the solution is ideal. Equations (9.216) and (9.217) lead to the equality:

$$L_{11} = \frac{C_1}{RT} D_1 \tag{9.218}$$

which connects the phenomenological coefficient with the diffusion coefficient. For further details and various aspects of the phenomenological theory of diffusion, the reader is referred to specialized treatises (for example, S.R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics*, North Holland, Amsterdam, 1962).

9.15. Diffusion in Nonisothermal Systems

We shall first consider heat transfer that occurs in a system of homogeneous composition at negligibly small external forces F_γ. The production of entropy is given by relation (9.115):

$$\sigma_h = -J_h \frac{\text{grad } T}{T^2} \geqslant 0 \tag{9.219}$$

If we confine ourselves to the consideration of the heat flux in the x direction, we obtain:

$$\sigma_h = -J_h \frac{1}{T^2} \frac{\partial T}{\partial x} \tag{9.220}$$

It would be logical, from the viewpoint of the general method, to regard J_h as a flux (thermal energy) and $(1/T^2)\,(\partial T/\partial x)$ as a force (thermal affinity) and write the linear law in such a form:

$$J_h = -L_h \frac{1}{T^2} \frac{\partial T}{\partial x} \tag{9.221}$$

However, the requirement of consistency with Fourier's law

$$J_h = -l \frac{\partial T}{\partial x} \tag{9.222}$$

in which the thermal conductivity coefficient is constant or, at least, exhibits slight sensitivity with respect to temperature, compels us to put

$$L_h = lT^2 \tag{9.223}$$

On the other hand, with Fourier's law taken into account in considering relation (9.220), we obtain for the rate of entropy production:

$$\sigma_h = l \frac{1}{T^2} \left(\frac{\partial T}{\partial x} \right)^2 \tag{9.224}$$

Employing now l instead of L_h as a phenomenological coefficient, we must take the relation $-(1/T)(\partial T/\partial x)$ as a thermodynamic force instead of $-(1/T^2)(\partial T/\partial x)$, and J_h/T as a thermodynamic flux instead of J_h. Then, setting up, as before, the product (flux × × force), we find that

$$\sigma_h = (J_h/T)(1/T)(\partial T/\partial x) = J_h (1/T^2)(\partial T/\partial x)$$

The advantage of the use of constant or almost constant Onsager coefficients is particularly important in studies of parallel nonequilibrium processes.

Let us now consider the effects that arise from parallel (simultaneously occurring) processes of heat conduction and diffusion. We first define the molar velocity of motion u with the aid of the relation

$$uC = \sum_{\gamma} C_{\gamma} \omega_{\gamma} \tag{9.225}$$

where C_{γ} are the molar concentrations of the components which are equal to ρ_{γ}/M_{γ}.

If the rates of diffusion are expressed, as before [see Eq. (9.66)], in terms of the velocity difference

$$\Delta_{\gamma}^{u} = \omega_{\gamma} - \omega \tag{9.226}$$

then, as an analogue of relation (9.67), we obtain:

$$\sum_{\gamma} C_{\gamma} \Delta_{\gamma} = 0 \tag{9.227}$$

Taking account of the new expressions for the diffusion affinity [see Eqs. (9.208) and (9.209)], we can write the following relation for the rate of production of entropy arising from the transfer of heat and diffusion in a two-component system:

$$\sigma_t = J_h \operatorname{grad} \frac{1}{T} + \left(\frac{A_1^{*d}}{T} C_1 \Delta_1^u \right) + \left(\frac{A_2^{*d}}{T} C_2 \Delta_2^u \right) \tag{9.228}$$

Or, taking cognizance of Eq. (9.227) and also of Eq. (9.211), i.e., $A_2^{*d} = -(C_1/C_2)A_1^{*d}$, we transform (9.228) as follows:

$$\sigma_t = J_h \operatorname{grad}\frac{1}{T} + \left[\frac{1}{T}\left(1+\frac{C_2}{C_1}\right)A_2^{*d}C_2\Delta_2^u\right] \tag{9.229}$$

Let us now set up phenomenological relations for the diffusional and heat fluxes, assuming, according to Onsager, that the off-diagonal coefficients are equal, i.e., $L_{12} = L_{21}$:

$$C_2\Delta_2^u = \frac{L_{11}}{T}\frac{C}{C_1}A_2^{*d} + L_{12}\operatorname{grad}\frac{1}{T} \tag{9.230}$$

$$J_h = \frac{L_{21}}{T}\frac{C}{C_1}A_2^{*d} + L_{22}\operatorname{grad}\frac{1}{T} \tag{9.231}$$

where $C = C_1 + C_2$. Since, as follows from Eq. (9.209), in the absence of external forces the diffusion affinity is equal to the gradient of chemical potential, $A_\gamma^{*d} = -(\operatorname{grad}\mu_\gamma)_T$, and $\mu_\gamma = \mu_\gamma^\circ + RT\ln a_\gamma$, where a_γ is the activity of the component, we can write the following relation with N_2 denoting the mole fraction of the second component:

$$A_2^{*d} = -\left(\frac{\partial\mu_2}{\partial N_2}\right)\operatorname{grad}N_2 = -\frac{RT}{a_2}\frac{\partial a_2}{\partial N_2}\operatorname{grad}N_2 \tag{9.232}$$

Now the fluxes in (9.230) and (9.231) can be represented in the form:

$$C_2\Delta_2^u = -DC\operatorname{grad}N_2 - \frac{L_{12}}{T^2}\operatorname{grad}T \tag{9.233}$$

$$J_h = -\frac{L_{12}}{L_{11}}DC\operatorname{grad}N_2 - \frac{L_{22}}{T^2}\operatorname{grad}T \tag{9.234}$$

where

$$D = \frac{L_{11}R}{C_1a_2}\frac{\partial a_2}{\partial N_2}$$

These linear equations predict the coupling and mutual influence of two fluxes—two effects which are known as the Dufour effect and the thermodiffusion effect (the Soret effect). Let us consider these equations in greater detail. If there is initially no temperature gradient ($\operatorname{grad}T = 0$), Eq. (9.233) then gives an ordinary diffusion flux for systems without a temperature field. Here it is obvious that D is the diffusion coefficient. However, if $\operatorname{grad}N_2 \neq 0$, the onset of diffusion leads, in accordance with Eq. (9.234), to the appearance of an initial heat flux:

$$J_h = -\frac{L_{12}}{L_{11}}DC\operatorname{grad}N_2 \tag{9.235}$$

which produces a temperature gradient. This is known as the Dufour effect observed when two gases, which are initially at the same temperature, are mixed through interdiffusion. This effect has not yet been observed in liquids.

The existence of the Soret effect stems from the following considerations: if grad $N_2 = 0$ and grad $T \neq 0$. Eqs. (9.233) and (9.234) assume the form:

$$J_h = -l \,\text{grad}\, T \tag{9.236}$$

$$C_2\Delta_2^u = -\frac{L_{21}}{T^2}\,\text{grad}\, T \tag{9.237}$$

where l is the thermal conductivity coefficient equal to L_{22}/T^2. From Eq. (9.237) it follows that if a system of initial homogeneous composition is heated from one end and cooled from the other, there will appear diffusion and the particles of substance (2) will be concentrated at the heated end if $L_{12} > 0$ or at the cold end if $L_{12} < 0$. Thermodiffusion has been studied extensively and is employed for the separation of the uranium isotopes 235 and 238. The Soret effect has been detected in liquids, where it is stronger by an order of magnitude than in gases.

As an example of stationary states arising from thermal diffusion, let us consider a mixture composed of equal amounts of nitrogen and oxygen, placed in a flat-bottomed vessel. Suppose that the upper wall is kept at a temperature of 500°C, and the lower wall at 0°C. In the stationary state there will occur a partial separation of the mixture, the amounts of N_2 and O_2 at the upper wall being, respectively, 50.27 per cent and 49.73 per cent and 49.73 per cent and 50.27 per cent at the lower wall. Thus, the lighter component is concentrated at the warmer end.

9.16. Electrokinetic Effects

Using the methods of nonequilibrium thermodynamics in conjunction with the Onsager reciprocal relations, we can also consider the connection between the various electrokinetic effects that arise in a system in which either there is an electric potential difference or such a potential difference is developed by these effects.

Let us consider a system consisting of two vessels I and II joined by a porous wall or a capillary. The temperatures and concentrations (in mole fractions) are assumed to be equal throughout the entire system and the two phases differ only in pressure p and electrical potential φ. The production of entropy arising from the transport of matter from vessel I into vessel II is expressed by the folowing relation:

$$Td_iS = \sum_{\gamma} \tilde{A}_\gamma\, d\xi = \sum_{\gamma} \tilde{A}_\gamma\, dn_\gamma^{I} \geqslant 0 \tag{9.238}$$

where $\tilde{A}_\gamma$ is the electrochemical affinity defined as follows:

$$\tilde{A}_\gamma = \tilde{\mu}_\gamma^{I} - \tilde{\mu}_\gamma^{II} = \mu_\gamma^{I} - \mu_\gamma^{II} + Z_\gamma(\varphi^{I} - \varphi^{II}) \tag{9.239}$$

in which expression the electrochemical potential of substance γ in a given phase is defined as

$$\tilde{\mu}_\gamma = \mu_\gamma + Z_\gamma \varphi \qquad (9.240)$$

and Z_γ expresses the multiplicity of the ionic charge. Thus, the electrochemical affinity equals the sum of the chemical and electrical potential differences:

$$\tilde{\mathbf{A}}_\gamma = \Delta\mu_\gamma + Z_\gamma \Delta\varphi \qquad (9.241)$$

being determined for two vessels I and II. We now substitute this value of $\tilde{\mathbf{A}}_\gamma$ into Eq. (9.238), using the well-known relation $\partial\mu_\gamma/\partial p = \bar{v}_\gamma$ and assuming the partial molar volume of the component to be constant; the rate of entropy production will then be written as

$$T\frac{d_iS}{dt} = T\sigma_S = -\sum_\gamma \bar{v}_\gamma \frac{dn_\gamma^{\mathrm{I}}}{dt}\Delta p - \sum_\gamma Z_\gamma \frac{dn_\gamma^{\mathrm{I}}}{dt}\Delta\varphi \geqslant 0 \qquad (9.242)$$

We now determine the fluxes:

$$J_m = -\sum_\gamma \bar{v}_\gamma \frac{dn_\gamma^{\mathrm{I}}}{dt} \quad \text{and} \quad I = -\sum_\gamma Z_\gamma \frac{dn_\gamma^{\mathrm{I}}}{dt} \qquad (9.243)$$

where I is the electric current arising from the transfer of charges from I to II, and J_m is the net flux of matter, which may also be called the flux of volume. Combining Eqs. (9.242) and (9.243) leads to

$$\frac{d_iS}{dt} = J_m \frac{\Delta p}{T} + I\frac{\Delta\varphi}{T} \qquad (9.244)$$

and then we set up phenomenological equations of the form

$$I = L_{11}\frac{\Delta\varphi}{T} + L_{12}\frac{\Delta p}{T}; \quad J_m = L_{21}\frac{\Delta\varphi}{T} + L_{22}\frac{\Delta p}{T} \qquad (9.245)$$

Here, in accordance with the Onsager reciprocity theorem, $L_{12} = L_{21}$. Thus, we are dealing with two nonequilibrium processes—the transfer of matter under the influence of a pressure drop and the electric current arising from a potential difference. Besides, in accordance with Eq. (9.245), there may also appear mixed effects because of $L_{12} = L_{21} \neq 0$, which reflect the coupling of two nonequilibrium processes. We can distinguish a total of four effects accessible to experimental testing.

1. With electric current equal to zero, we obtain the potential of a flux of matter

$$\left(\frac{\Delta\varphi}{\Delta p}\right)_{I=0} = -\frac{L_{12}}{L_{11}} \qquad (9.246)$$

2. With the pressures in the vessels being initially equal ($\Delta p = 0$) we have the *electro-osmotic effect*:

$$\left(\frac{J_m}{I}\right)_{\Delta p=0} = \frac{L_{21}}{L_{11}} \tag{9.247}$$

3. If the flux of matter J_m is equal to zero, from relation (9.245) we define the *electro-osmotic pressure* that hinders the generation of a flux:

$$\left(\frac{\Delta p}{\Delta \varphi}\right)_{Jm=0} = -\frac{L_{21}}{L_{22}} \tag{9.248}$$

4. In the absence of a potential difference between the two parts of the system ($\Delta\varphi = 0$) there appears a *flow of electric current*:

$$\left(\frac{I}{J_m}\right)_{\Delta \varphi=0} = \frac{L_{12}}{L_{21}} \tag{9.249}$$

It is easy to see that the application of the Onsager relation $L_{12} = L_{21}$ allows us to establish the relationship between the osmotic effect and the flow effect:

$$\left(\frac{\Delta \varphi}{\Delta p}\right)_{I=0} = -\left(\frac{J_m}{I}\right)_{\Delta p=0} \tag{9.250}$$

$$\left(\frac{\Delta p}{\Delta \varphi}\right)_{Jm=0} = -\left(\frac{I}{J_m}\right)_{\Delta \varphi=0} \tag{9.251}$$

Relation (9.250) known as the Zaxen formula has been derived on the basis of a pure kinetic treatment of the problem. However, this relation holds only for a simplified model of the membrane that divides two phases; for example, if the membrane is identified with a capillary of constant cross-section. The importance of the thermodynamic approach lies in that it is independent of the membrane model—it holds for any membrane or porous partition.

The above example is given in order to provide the reader with an idea of what kind of information can be obtained by means of the methods of nonequilibrium thermodynamics. Although these methods are insufficient for calculations of thermodynamic coefficients, they nevertheless enable us to establish the relation between phenomena that seem to be quite independent. There also exist a large number of other effects, such as the Zeeman effect, the Peltier effect, and also the thermo-osmotic and thermomechanical effects, the Knudsen effect, etc., which are also dealt with by the methods of nonequilibrium thermodynamics.

Appendixes

APPENDIX 1. Physical Constants and Some Conversion Factors

Ice point (0°C)	273.150°K
Triple point of H_2O, defined	273.16000°K
Thermochemical calorie (cal)	4.1840 J
Acceleration of gravity, standard	9.80665 $m \cdot s^{-2}$
Atmosphere (defined, 760 mm Hg under standard conditions)	101,325 m^{-2} or 1.013250 × 10^6 $dynes \cdot cm^{-2}$
Mole	Amount of substance that contains as many elementary entities as there are carbon atoms in 0.012 kg of carbon-12
Speed of light, c	299,792,458(12) $m \cdot s^{-1}$ or 2.997925 × 10^{10} $cm \cdot s^{-1}$
Gas constant, R	8.31441(26) $J \cdot mol^{-1} \cdot K^{-1}$ 82.0568(26) × 10^{-6} $m^3 \cdot atm \cdot mol^{-1} \cdot K^{-1}$ 1.98719(6) $cal \cdot mol^{-1} \cdot K^{-1}$
Planck's constant, h	6.626176(36) × 10^{-34} $J \cdot s$
Elementary charge, e	1.6021892(46) × 10^{-19} C or 4.803242 esu
Boltzmann constant, k	1.380662(44) × 10^{-23} $J \cdot K^{-1}$
Avogadro's number, N_A	6.022045(31) × 10^{23} mol^{-1}
Electron rest mass, m_e	9.109534(47) × 10^{-31} kg
Proton rest mass, m_p	1.6726485(86) × 10^{-27} kg
Faraday constant, $F = N_A e$	96484.56(27) $C \cdot mol^{-1}$
Volume of ideal gas (1 atm, 273.15°K), v_m	22.41383(70) × 10^{-3} $m^3 \cdot mol^{-1}$
Bohr radius, a_0	0.52917706(44) × 10^{-10} m
ln 10	2.302585
$R \ln x$	4.5758 $\log_{10} x$ $cal \cdot mol^{-1} \cdot K^{-1}$
298.15 $R \ln x$	1364.3 $\log_{10} x$ $cal \cdot mol^{-1}$

The atomic mass unit is defined as exactly 1/12 the mass of a carbon-12 atom.

APPENDIX II. **Table of Debye Functions for Heat Capacity** $C_v/3R = f\,(\theta_D/T)$

$\left[\text{at values of } \frac{\theta_D}{T} \geqslant 1.6,\ \frac{C_v}{3R} = 77.927 \left(\frac{T}{\theta_D}\right)^3\right]$

θ_D/T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.0	1.0000	0.9995	0.9980	0.9955	0.9920	0.9876	0.9822	0.9759	0.9687	0.9606	0.9517
1.0	0.9517	0.9420	0.9315	0.9203	0.9085	0.8960	0.8828	0.8692	0.8550	0.8404	0.8254
2.0	0.8254	0.8100	0.7943	0.7784	0.7622	0.7459	0.7294	0.7128	0.6961	0.6794	0.6628
3.0	0.6628	0.6461	0.6296	0.6132	0.5968	0.5807	0.5647	0.5490	0.5334	0.5181	0.5031
4.0	0.5031	0.4883	0.4738	0.4595	0.4456	0.4320	0.4187	0.4057	0.3930	0.3807	0.3686
5.0	0.3686	0.3569	0.3455	0.3345	0.3237	0.3133	0.3031	0.2933	0.2838	0.2745	0.2656
6.0	0.2656	0.2569	0.2486	0.2405	0.2326	0.2251	0.2177	0.2107	0.2038	0.1972	0.1909
7.0	0.1909	0.1847	0.1788	0.1730	0.1675	0.1622	0.1570	0.1521	0.1473	0.1426	0.1382
8.0	0.1382	0.1339	0.1297	0.1257	0.1219	0.1182	0.1146	0.1111	0.1078	0.1046	0.1015
9.0	0.1015	0.09847	0.09558	0.09280	0.09011	0.08751	0.08500	0.08259	0.08025	0.07800	0.07582
10.0	0.07582	0.07372	0.07169	0.06973	0.06783	0.06600	0.06424	0.06253	0.06087	0.05928	0.05773
11.0	0.05773	0.05624	0.05479	0.05339	0.05204	0.05073	0.04946	0.04823	0.04705	0.04590	0.04478
12.0	0.04478	0.04370	0.04265	0.04164	0.04066	0.03930	0.03878	0.03788	0.03701	0.03617	0.03535
13.0	0.03535	0.03455	0.03378	0.03303	0.03230	0.03160	0.03091	0.03024	0.02959	0.02896	0.02835
14.0	0.02835	0.02776	0.02718	0.02661	0.02607	0.02553	0.02501	0.02451	0.02402	0.02354	0.02307
15.0	0.02307	0.02262	0.02218	0.02174	0.02132	0.02092	0.02052	0.02013	0.01975	0.01938	0.01902

APPENDIX III. Coefficients M_i for Calculation of ΔG°_T According to Formula (5.117)

T, °K	M_0	$M_1 \cdot 10^{-3}$	$M_2 \cdot 10^{-6}$	$M_{-2} \cdot 10^5$
300	0.0000	0.0000	0.0000	0.0000
400	0.0392	0.0130	0.0043	0.0364
500	0.1133	0.0407	0.0149	0.0916
600	0.1962	0.0759	0.0303	0.1423
700	0.2794	0.1153	0.0498	0.1853
800	0.3597	0.1574	0.0733	0.2213
900	0.4361	0.2012	0.1004	0.2521
1000	0.5088	0.2463	0.1134	0.2783
1100	0.5765	0.2922	0.1652	0.2988
1200	0.6410	0.3389	0.2029	0.3176
1300	0.7019	0.3860	0.2440	0.3340
1400	0.7595	0.4336	0.2886	0.34835
1500	0.8141	0.4814	0.3362	0.3610
1600	0.8665	0.5296	0.3877	0.3723
1700	0.9162	0.5780	0.4424	0.3824
1800	0.9635	0.6265	0.5005	0.3915
1900	1.0090	0.6752	0.5619	0.3998
2000	1.0525	0.7240	0.6265	0.4072
2100	1.0940	0.7730	0.6948	0.4140
2200	1.1340	0.8220	0.7662	0.4203
2300	1.1730	0.8711	0.8411	0.4260
2400	1.2100	0.9203	0.9192	0.4314
2500	1.2460	0.9696	1.0008	0.4363
2600	1.2800	1.0189	1.0856	0.4408
2700	1.3140	1.0683	1.1738	0.44505
2800	1.3460	1.1177	1.2654	0.4490
2900	1.3775	1.1672	1.3603	0.4527
3000	1.4080	1.2166	1.4585	0.4562

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